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MINING AND WESTERN WORLD SOURCES OF VANADIUM*

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(Revised version received September 29th, 1961)

INTRODUCTION

Production and consumption of vanadium continues to rise both in the United States and abroad. World reserves are so vast as to prevent appraisal, while unneeded vanadium continues to be dissipated in tailings or stockpiled due to the high cost of mining and extractive metallurgy. Meanwhile, research and development forges ahead in search of new recovery techniques and additional uses of vanadium and its derivatives.

Vanadium is the eighth most abundant metal in the earth's crust; however, its natural occurrence does not favor high concentration. It is more often found in such complex mineral associations as vanadinite, descloizite, patronite, carnotite, and roscoelite. It is produced in conjunction with uranium, iron, titanium, aluminum, and lead. Future sources of vanadium may be the vanadium-bearing green micas and various base metal vanadates, asphaltite, petroleum, coal, and bauxite deposits.

TABLE I

IMPORTANT VANADIUM MINERALS

Vanadinite	$3\ PbO \cdot V_2O_5 \cdot PbCl_2$
Descloizite	$4(Pb,Zn)O \cdot V_2O_5 \cdot H_2O$
Cuprodescloizite	$4(Pb,Cu,Zn)O \cdot (V,As)_2O_5 \cdot H_2O$
Mottramite	$5(Cu,Pb)O \cdot V_2O_5 \cdot 2\ H_2O$
Tyuyamite	$CaO \cdot 2\ UO_3 \cdot V_2O_5 \cdot 4\ H_2O$
Hewetite Metahewetite	$CaO \cdot 3\ V_2O_5 \cdot 9\ H_2O$
Carnotite	$K_2O \cdot 2\ UO_3 \cdot V_2O_5 \cdot 3\ H_2O$
Roscoelite	$H_8K(Mg,Fe)(Al,V)_4 \cdot 15\ H_2O$

U.S. PRODUCTION AND POTENTIAL

The United States is the largest producer and consumer of vanadium. From 1910 through 1959 over 72,300 tons of ore were mined. The bulk of the vanadium output was a by-product of the accelerated uranium-concentrate production program in operation between 1952 and 1956. Today, vanadium continues to be a by-product or co-product of the carnotite ores being mined for uranium.

* Paper presented at the Symposium on Vanadium of the Electrothermics and Metallurgy Division of the Electrochemical Society, May 2, 1960, Chicago, Illinois.

Used domestically, vanadium is a minor alloy that toughens steel axles, pistons, crankshafts and pins. High-speed steels contain 4–5% of vanadium. Vanadium helps to remove oxygen and nitrogen from steels, giving a more uniform grain size. It has found a new outlet as a catalyst and is used to a small extent in the electrical, chemical, ceramic, paint, dye, and printing industries.

Carnotite ores of the Colorado Plateau are the most important domestic source of vanadium. Most of the deposits occur in sandstone as vanadium oxides or silicates, or vanadates of uranium and calcium. The minerals occupy pore spaces in the sandstone which form flat-lying tabular ore bodies. The method of mining depends on the depth and extent of the ore body. Shallow overburden enables open pit methods. Ore body outcroppings permit tunneling. Only a sizeable and rich deposit could warrant sinking a shaft. The carnotite ores are the major source of mill feed for uranium–vanadium production. Mineral content of the ore runs high, usually 1.5–2% of V_2O_5. Treatment for the extraction and recovery of the metal is the salt roast–aqueous leach–red cake process. The calcined sand tailings are leached with sulfuric acid to extract additional vanadium and uranium. After further separation and refinement commercial concentrates are produced. The potential capacity of the present operating vanadium–uranium mills is estimated at 8,000 tons of V_2O_5 per year. In recent years these concentrates have been marketed at \$0.98–\$1.25 per pound of contained V_2O_5. Known reserves of the carnotite ores of the Colorado Plateau are

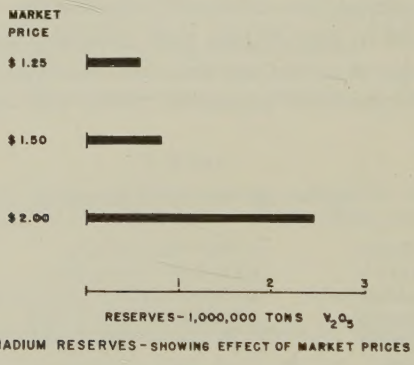

Fig. 1.

large and are estimated to contain 50,000 short tons of recoverable V_2O_5 averaging 1.65%. Potential reserves are even greater but will be increasingly more costly to find and develop.

The roscoelite or vanadium-mica ores have been another important domestic source of vanadium since 1910. They are found near Rifle and around Placerville, Colorado, two distinct regions of the state but in the same Entrada formation. They are low lime content ores and quite amenable to the salt roast–water leach process. It is estimated that 2,000 tons per year of V_2O_5 could be produced from roscoelite ores on the Colorado Plateau. Known reserves are estimated to contain 6,000 tons of recoverable V_2O_5 averaging 1.2–2%, while potential reserves run several times higher.

Titaniferous magnetites are yielding vanadium in Iron Mountain, Wyoming and the Lake Sanford district of New York. The Wyoming deposits were discovered in 1853 but have not attracted commercial exploitation because the magnetite and ilmenite minerals are so finely intergrown in the major occurrences. The high-grade material averages 0.6% of V_2O_5 and reserves are estimated at 70,000 short tons. Low-grade ore reserves may total 20,000,000 tons but will never be mined unless demand rises and costs fall. New York deposits of titaniferous magnetites are being mined primarily for titanium. The by-product magnetite contains about 0.70% of V_2O_5 which is not being recovered. Were it recovered, approximately 550,000 tons of V_2O_5 would become available.

Vanadiferous shales afford a large resource of vanadium in south-eastern Idaho and western Wyoming. The deposit is not being mined but reserves are estimated at three times the world's total production of vanadium, or approximately 550,000 short tons.

Western phosphate smelters produce an estimated 20,000 tons of ferrophosphorus annually. This by-product yields 7–8% of V_2O_5. Most of the United States' ferrophosphorus is exported to European markets. Were it sustained in the United States, approximately 1,250 tons of V_2O_5 could be recovered each year.

WORLD PRODUCTION AND POTENTIAL

Western world production of vanadium is limited to the United States, Finland, and the Union of South Africa. The world's largest single deposit of vanadium, and asphaltite vein in Peru, has been depleted and operations ceased in 1955. For a time, the United States was the only large-scale producer. Then in 1957 two new recovery operations commenced and now supply most of Europe.

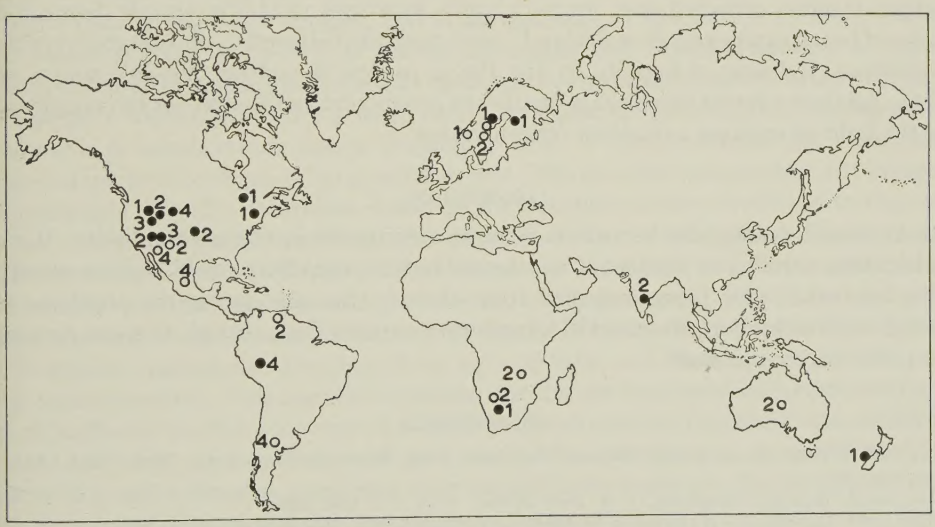

Fig. 2. The western world's vanadium reserves (V_2O_5).

Size of deposit	*Grade*	
1 — 100,000 tons, or more	1% or more	V_2O_5
2 — 25,000–100,000 tons	0.5 –1.0%	V_2O_5
3 — 1,000– 25,000 tons	0.25–0.5%	V_2O_5
4 — less than 1,000 tons	less than 0.25%	V_2O_5

Otanmaki, Finland is the only major European producer of vanadium concentrate. The titaniferous magnetite ore contains 35% of magnetite, 28% of ilmenite and around 0.46% of V_2O_5. Vanadium concentrate production is limited by magnetite recovery, which is restricted by the ore-hoisting capacity of the shaft. If market needs for magnetite and vanadium should increase additional shafts could be installed and production could be doubled; this economic incentive is, however, unlikely. The Otanmaki Company is producing 1,100 short tons of V_2O_5 per year with possible reserves amounting to 325,000 short tons, enough to maintain present production for 50 years. The largest consumers of Otanmake vanadium concentrates are the ferro-vanadium producers of West Germany, Sweden, and France.

Witbank, Transvaal, in the Union of South Africa is the site of a new mill producing 125,000 pounds of V_2O_5 per month with an ultimate capacity of 250,000 pounds. Expected recovery is 1,400 short tons of V_2O_5 per year. The outcrops of weathered titaniferous magnetites are being mined in open cuts with a truck-mounted electro-magnetic crane. The deposit is roughly 100 miles in diameter and covers an area of 12,000 square miles. The ore occurs in thick sheets at different horizons in the rock mass. It is assumed these layers extend to great depths behind their outcrops. The vanadium content of the ore runs as high as 1.5% of V_2O_5. Reserves are sufficient to support numerous operations if markets were available.

The Province of Quebec in Canada has abundant titaniferous magnetite deposits which are now being mined for titanium and iron. Vanadium pentoxide is not being recovered but assuming normal vanadium content the deposits represent a large reserve of the metal.

Other potential but unlikely sources are the recovery of vanadium from dichromate production, from refining lead vanadate minerals and from high vanadium soots and carbon residues collected from burning South American vanadiferous oils. Some 300 miles of beach sand along New Zealand's west coast are believed to contain recoverable vanadium. Refining of bauxite by the Bayer process is another possible source of V_2O_5. All these sources represent insignificant production and should not be considered in the light of existing vanadium concentration.

CONCLUSIONS

An increased demand for vanadium may be anticipated in the steel industry. Were production costs to be lowered it is reasonable that vanadium could replace certain alloying metals now being imported from abroad, thus alleviating the problems of waste and stockpiling. Reserves of vanadium are more than enough to meet present and near-future demands.

REFERENCES

ALAN M. BATEMAN, *Economic Mineral Deposits*, John Wiley & Sons, Inc., New York, 1955, p. 603–605.

PHILLIP M. BUSCH, Vanadium, *U.S. Bur. Mines, Bull. No. 585*, 1960.

PHILLIP M. BUSCH AND KATHLEEN W. MCNULTY, Vanadium, *Bureau of Mines Minerals Yearbook*, Vol. 1, 1959.

Report on Vanadium by Raw Material Group, Natl. Acad. of Science, 1959.

THE TREATMENT OF VANADIUM ORES FOR THE RECOVERY OF VANADIUM PENTOXIDE*

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(Revised version received September 29th, 1961)

INTRODUCTION

Carnotite ores, roscoelite ores, titaniferous magnetite, shales, and phosphates are being treated to recover vanadium as vanadium pentoxide, V_2O_5. However, many other vanadiferous ore types are *not* being treated for the recovery of vanadium. These reserves are substantial and afford distinct economic possibilities.

GENERAL TREATMENT OF ORES

Vanadium pentoxide and vanadium concentrates are products of many distinct ore classes. Geologic characteristics peculiar to each vanadium deposit greatly influence the metallurgical recovery process. Widespread research has taken place since 1910 into the basic metallurgical treatments for recovering vanadium from its ores and from vanadiferous slags, sludges, and other materials. Vanadium is currently being recovered at a rate of 65–85% of the total ore contained. Nominal amounts of vanadium can be economically recovered by hydrometallurgical methods following roasting. To achieve higher recoveries a more costly and difficult metallurgical treatment is required. A beneficiation step is frequently used to preconcentrate the vanadium minerals prior to hydrometallurgical treatment. This provides an economic advantage. An example of such a treatment would be the flotation scheme developed in 1950 to treat a complex lead–vanadium ore occurring in the Abenab West deposit near Grootfontain in Southwest Africa. The mineral was a complex vanadinite–descloizite –cerrusite ore and was treated by flotation, using potassium ethyl xanthate and potassium amyl xanthate as collectors with careful pH control. This method produced a vanadium concentrate assaying about 14% of V_2O_5 and containing about 86% of the total vanadium. This material was then suitable for treatment by hydrometallurgical methods for the recovery of a high-grade vanadium pentoxide concentrate.

The salt roast–aqueous leach–red cake precipitation process is most widely used in extracting and recovering vanadium from vanadiferous materials. Figure 1 illustrates the extraction process briefly and shows an alternate step for higher-grade ores. The raw material is ground for passage through a 10-mesh being mixed with an appropriate percentage of salt. The mixture is roasted in a hearth furnace or rotary kiln at 800–850°C for 1–2 h, thus producing water-soluble sodium vanadates. The

* Paper presented at the Symposium on Vanadium of the Electrothermics and Metallurgy Division of the Electrochemical Society, May 2, 1960, Chicago, Illinois.

alternate circuit, which effects a joint extraction of vanadium and uranium, requires the quenching of hot calcine in a sodium carbonate–sodium bicarbonate solution. The vanadium and uranium are separated by precipitation of uranium as an artificial carnotite (sodium uranylvanadate) which is fused with salt, sawdust, or fuel oil to give a water-soluble vanadium salt and the insoluble black oxide of uranium, UO_2.

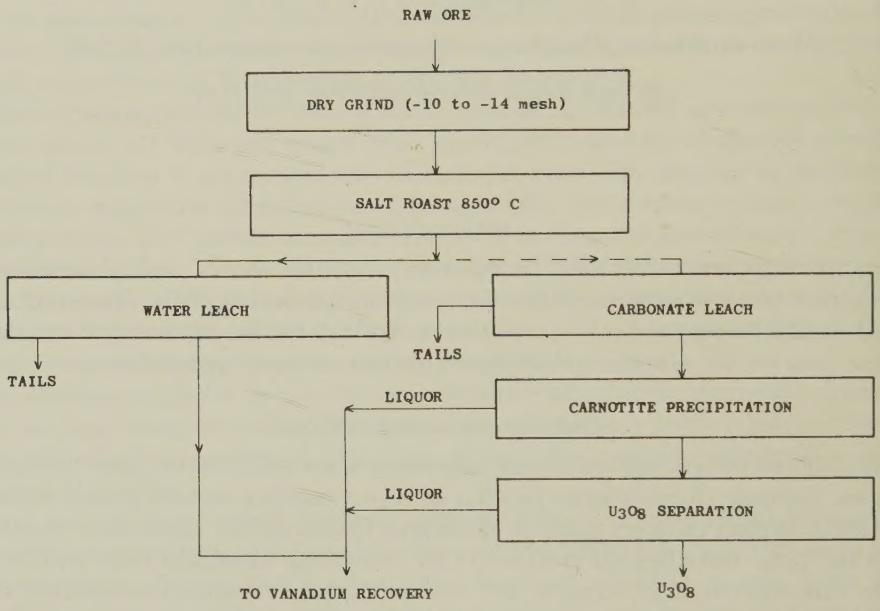

Fig. 1.

Vanadium is then recovered from the solution. Recovery by this method is usually 65–85% effective, depending on the roasting conditions. Additional vanadium can be recovered from the calcine by using an acidified leach. Some minerals require finer grinding, while others give better results by the addition of sodium carbonate to the salt.

The recovery process is outlined in Fig. 2. Any reduced vanadium in the liquor is oxidized by the addition of sodium chlorate. Sulfuric acid is added to adjust the pH to around 2.5–2.7. Red cake or sodium polyvanadate forms and prolonged agitation at a temperature of 95°C precipitates the vanadium. The red cake is filtered, washed and then melted in a direct-fired furnace. The melt drops onto a flaker yielding black, fused V_2O_5, usually about 86% pure. A higher purity product is obtainable by taking the filtered red cake and redissolving it in ammonia forming ammonium meta- or poly-vanadate precipitates. Fusion of these ammonium salts yields 98–99% V_2O_5. With market specifications requiring a minimum concentration of 86% more vanadium producers are adopting the ammonia method.

The salt roast–water leach treatment process is hindered by the formation of calcium vanadates and the co-precipitation of phosphorus with the red cake. Interference by calcium can be minimized by acidifying the ore or slag with sulfuric acid

before roasting or by fixing the calcium as calcium sulphate with the addition of pyrite to the roast feed. Calcium phosphates are converted to water-soluble phosphates in salt roasting or acid leaching. Excessive phosphorus can be removed by fractional crystallization or by precipitation prior to vanadium recovery.

The sulfuric acid or pugging treatment is very effective in recovering vanadium from

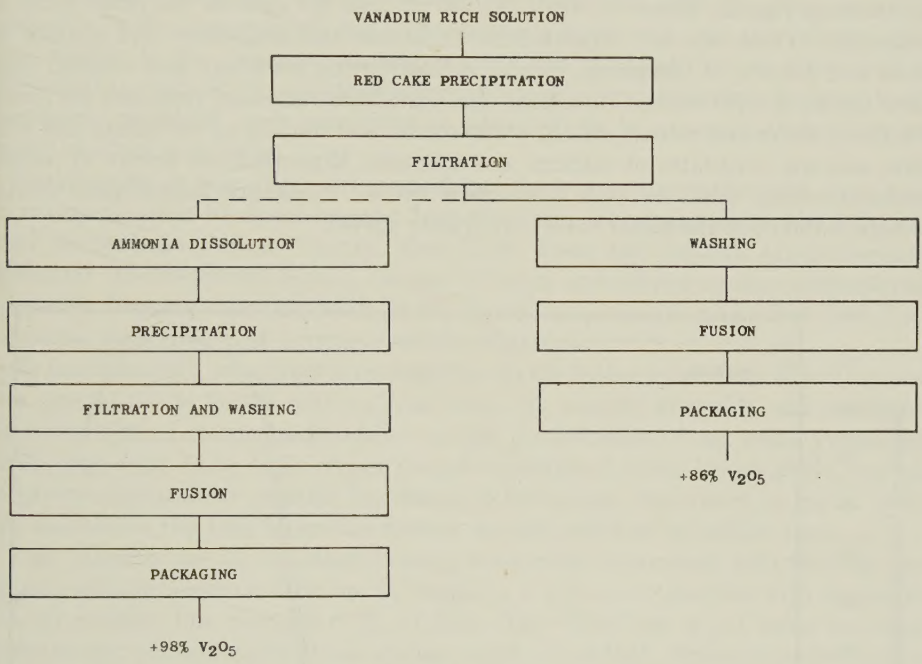

Fig. 2.

many ores. A leach with concentrated sulfuric acid or a sulfuric acid cure can render as much as 90% of the contained vanadium in some ores. However, the subsequent liquid–solid separations may be difficult and the presence of impurities greatly complicates vanadium recovery.

A pugging treatment usually involves mixing the finely divided ore with an amount of acid necessary to give the desired degree of acidity in the leach liquor. This averages 100–300 pounds of sulfuric acid per ton of ore. The acidified mass is moistened with water equal to 10% of the weight of the dry ore. The mixture is allowed to cure for a time sufficient to render 90–95% of the vanadium soluble. To assist dissolution, sodium silicofluoride or other reagents are added at a ratio of 0.1–0.2 pounds per ton of ore. Curing temperatures range from 60–100°C. The pugged material is then water leached for approximately an hour at a liquid–solid ratio of 1 : 1. A pH of the liquor is maintained that will facilitate introduction into a resin or solvent ion exchange circuit. Handling of this pugged material can be eliminated by leaching the ore at a pH of 0.5 or lower for 16–24 hours. However, in both cases the ion exchange technique is used to recover the vanadium.

TREATMENT OF SPECIFIC ORES

Vanadium ores are classified according to their genetic and geochemical relationships. The mineral associations of the ore determine which treatment of vanadium recovery will be used.

Carnotite ores are the primary source of vanadium in the United States and the world. Occurrence in the United States is confined to the Utah, Colorado, New Mexico, and Arizona regions. However, the Colorado plateau far exceeds the other areas in production. These ores are deposited in sandstones and limestones and contain as much as 1.5–2.0% of vanadium. Similar ores occurring elsewhere may contain only a few tenths of a per cent of vanadium. The vanadium–uranium type ores are found in all four states and consist mainly of the oxides and silicates of vanadium and uranium and the vanadates of calcium and uranium. Mineralization occurs in porous sandstone which tends to form tabular ore bodies. These ore bodies have similar geologic habits but the metal values are widely varied.

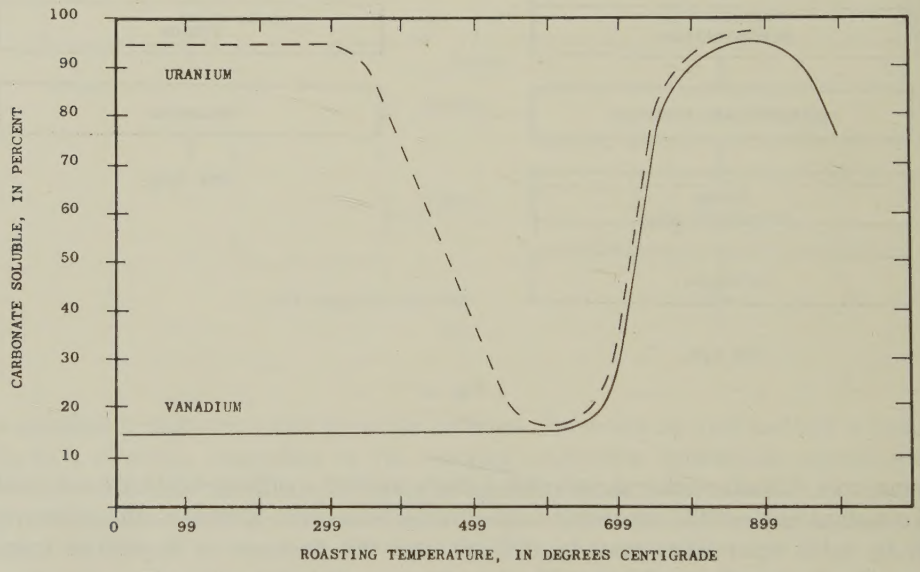

Fig. 3. (After A. C. RICHARDSON *et al.*, AEC-BMI-JOS-195-1949.)

Carnotite ores are usually treated by the salt roast–water leach process. The calcined vanadium tailings are leached with sulfuric acid to extract uranium and additional vanadium for commercial use. In recent years the fused vanadium pentoxide concentrate produced by plants treating carnotite ores has been marketed at a price ranging from \$0.98 to \$1.25 per pound of contained V_2O_5.

A new source of vanadium is arising from uranium plants employing a carbonate circuit. Vanadium content of the ore averages only 0.05%, but recirculation of the plant liquors nevertheless enables concentration to be effected. This step has become essential in order to meet yellow cake specifications. In Grants, New Mexico, uranium operators are considering a soda ash roast and water leach of yellow cake to remove

the vanadium. Production from this source totals approximately 30 tons of V_2O_5 per month for all plants.

The roscoelite or vanadium mica ores have been an important source of vanadium since 1910. They occur in the Entrada formation near Rifle, Colorado and a group of deposits around Placerville, Colorado, two distinct areas of the state. These deposits have never been assessed and appraisal would be difficult even today.

The roscoelite ores are low lime vanadium muscovite deposits. They are quite amenable to the conventional salt roast–aqueous leach–red cake precipitation process. Similar to the uranium–vanadium ores, they will yield any uranium and an additional 10–15% of the vanadium after a dilute acid leach following the water leach. Vanadium produced from roscoelites is estimated to be approximately $1.35 per pound of contained V_2O_5.

The titaniferous magnetites yield vanadium which is in association with iron. Such occurrences are to be found around Iron Mountain, Wyoming and in the Tahawas, Lake Sanford area, Essex County, New York. These two deposits are geologically dissimilar. The Wyoming deposit consists of lenses and tabular bodies of titaniferous magnetite forming dike-like zones in the anorthosite country rock. The New York deposit is associated with intrusive masses of gabbro.

As much as 0.6% vanadium is recovered from the higher grade Iron Mountain ores. The ground ore is mixed with 15% of soda ash, roasted at 950°C, and vanadium extracted with a water leach subject to the precipitation of red cake. Production costs range from $1.65 to $2.00 per pound of contained V_2O_5. Lower grade ores can be preconcentrated by suitable beneficiation techniques, but result in higher costs. Ore reserves in the Iron Mountain district are estimated at 12 million tons.

The Tahawas ore is vanadium-bearing magnetite intergrown with ilmenite and various silicate minerals. The ore is mined as a source of titanium with magnetite as a by-product but averages 0.5% of V_2O_5. This vanadium is not being recovered from the ore, yet represents about 450,000 short tons of V_2O_5. Research by the National Lead Company has produced a method for recovering vanadium from the magnetite concentrates. The ore is ground to a —200-mesh size and compressed into pellets containing 3–5% of salt and 6–10% of soda ash. The pellets are roasted at 950°C and water-leached in the presence of stack gases, which served to fix the aluminum in the leached cake. The vanadium is then recovered by the conventional red cake precipitation method. Recoveries range from 75 to 85% of the vanadium in the concentrate.

Shales occurring in the Idaho and Wyoming phosphatic shale member of the phosphoria formation are known to contain a high concentration of vanadium with trace amounts of molybdenum, nickel, and selenium. Reserves there are estimated at 550,000 short tons of V_2O_5. Investigations by the U.S. Bureau of Mines branch in Salt Lake City, Utah, conclude that 60–65% of the vanadium could be recovered from these shales. Metallurgical treatment was found to vary with the phosphorus content of the ore. Shales containing 1% of V_2O_5 and 2–3% of P_2O_5 were roasted with about 15% by weight of salt and several percent of pyrite then subjected to the water leach–red cake treatment. Some shales gave high extraction of vanadium, but the initial precipitate had to be redissolved and the resulting solution purified prior to the vanadium reprecipitation. After baking, the ores high in phosphates were salt roasted or treated with sulfuric acid to remove the organic material, thus, rendering

the vanadium soluble. The acid leach dissolved both the vanadium and phosphorus of which the latter was recovered by the Anaconda phosphatovanadic acid precipitation process.

Western phosphates are found to contain a generous reserve of vanadium. Of the thousands of tons of phosphate rock treated annually for the production of phosphate rock fertilizers, over 70% of the contained vanadium is rendered soluble and could be recovered.

Phosphate rock contains up to 0.3% of V_2O_5. When concentrated in the electric furnace, the ferrophosphorus by-product contains 7% of V_2O_5. The U.S. Bureau of Mines has developed a method of recovering as much as 90% of the vanadium from the by-product. It involves grinding the ferrophosphorus to a —100-mesh, mixing with sodium carbonate and salt in the weight ratios of 1 : 1 and 4 : 1 respectively, roasting at 800°C and water leaching the extracted calcine. Final vanadium recovery was done by the red cake method.

In 1923 the Anaconda Company developed a process to recover soluble vanadium in their phosphoric acid plant. Until 1954 when operations ceased they produced 150 tons of V_2O_5 annually. The phosphoric acid solution was concentrated by evaporation and clarification. The vanadium in the solution was oxidized with sodium chlorate to form the insoluble phosphatovanadic acid precipitate. The yellow crystalline precipitate, contaminated with aluminum, iron, phosphorus and other impurities, was removed and combined with soda ash and calcium chloride. The resulting soluble sodium vanadates and insoluble calcium phosphate were treated carefully with milk of lime to remove remaining impurities. This treatment left a substantially pure vanadium solution suitable for red cake precipitation. It is estimated to have produced a vanadium concentrate which sold for $1.25 to $1.50 per pound of V_2O_5.

CONCLUSION

Domestic and foreign production of vanadium revolves around the classic method of making the vanadium water-soluble by formation of sodium vanadates. The flowsheets are complicated by a need for the production of a more high purity product, by the co-recovery of additional values, and by the use of auxiliary circuits to achieve recoveries greater than 85% of the vanadium. It is considered unlikely that cheaper methods of producing vanadium pentoxide will be developed in the near future; however, the price may fall if consumption is materially increased.

MINERALOGY AND GEOCHEMISTRY OF VANADIUM IN THE COLORADO PLATEAU*,**

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(Received February 23rd, 1961)

SUMMARY

The chief domestic source of vanadium is uraniferous sandstone in the Colorado Plateau. Vanadium is 3-, 4-, or 5-valent in nature and, as oxides or combined with other elements, it forms more than 40 minerals in the Plateau ores. These ores have been studied with regard to the relative amounts of vanadium silicates and oxide-vanadates, uranium–vanadium ratios, the progressive oxidation of black low-valent ores to high-valent carnotite-type ores, and theories of origin.

INTRODUCTION

This paper is a short summary of some highlights of the mineralogy and geochemistry of vanadium in recent years. Emphasis is placed on the Colorado Plateau which is the chief source of vanadium in the United States. In Colorado, vanadium was produced only as a by-product of uranium and radium, from the time of the discovery of carnotite [$K_2(UO_2)_2V_2O_8 \cdot 3\ H_2O$] in 1898 until 1923, when uranium production ceased owing to the development of large uranium deposits in the Belgian Congo. In 1936 production of vanadium for itself first became important in Colorado[1]. Since World War II vanadium production has been associated once more with that of uranium. Through the intensive investigation of the uranium deposits for the development of atomic energy much has been learned about the mineralogy and geochemistry of vanadium.

Many articles and reports on various aspects of vanadium (its occurrence, mineralogy, crystal chemistry, geochemistry, and origin of the deposits) in the Colorado Plateau have been published recently. Considerable data and many literature references are given in a volume *"Geochemistry and Mineralogy of the Colorado Plateau Uranium Ores"* compiled by GARRELS AND LARSEN[2]. In this paper I have summarized some of the work by FISCHER[3], EVANS[4], GARRELS[5], FOSTER[6], HATHAWAY[7], CHRIST[5] and WEEKS[8], from GARRELS AND LARSEN.

GEOCHEMISTRY

Although our chief domestic source of vanadium is in deposits in sandstone in the Colorado Plateau, vanadium is found in several other types of geochemical environments. In a summary of types of vanadium deposits FISCHER[3] points out that vanadium also occurs in magmatic iron ores such as the vanadium-bearing magnetite–

* Publication authorized by the Director, U.S. Geological Survey.

** Paper presented at the Symposium on Vanadium of the Electrothermics and Metallurgy Division of the Electrochemical Society, May 2, 1960, Chicago, Illinois.

ilmenite deposits near Sanford Lake in the Adirondack Mountains of New York; in sedimentary iron ores where vanadium is sometimes a by-product; in vanadates of base metals as in the Mammoth area, Arizona; in phosphate rock as in the Paris–Bloomington area of Idaho; and as a by-product from soot or ash of some natural carbonaceous material.

Among the elements of the earth's crust vanadium is one of the more abundant trace elements. It is listed as number 22 by MASON[9] and is less abundant than Fe, Mn, and Cr but more abundant than Ni, Zn, Cu, and Pb (Table I). Some other estimates of abundance have listed vanadium as high as 0.015 or 0.02%.

TABLE I

ABUNDANCE OF CERTAIN ELEMENTS IN THE EARTH'S CRUST[9]

Order	*Element*	*Abundance (%)*
4	Fe	5.0
12	Mn	0.1
19	Cr	0.02
22	V	0.011
23	Ni	0.008
24	Zn	0.0065
27	Cu	0.0045
34	Pb	0.0015

The general geochemical character of vanadium according to RANKAMA AND SAHAMA[10] is lithophile with some siderophile tendency and a distinct biophile trend. Since vanadium occurs in three stable oxidation states (3^+, 4^+ and 5^+) in nature and forms a number of complex ions, there are many vanadium minerals as well as extensive possibilities of diadochic substitution of various elements by vanadium in mineral structures. In igneous rocks vanadium usually does not form independent minerals but is concealed in the structure of other minerals where V^{4+} may replace Ti^{4+}, Fe^{3+}, or Al^{3+}. Vanadium tends to become concentrated in basic igneous rocks. Traces of vanadium are common in sedimentary rocks and the oxidation state may be 3^+, 4^+, or 5^+ depending upon the oxidation potential of the sedimentary environment; V^{5+} and $^{4+}$ are most common and V^{3+} is generally limited to association with organic matter buried in the sediments.

MINERALOGY AND CRYSTAL CHEMISTRY

Since vanadium rarely occurs in separate minerals in igneous rocks, most of the vanadium minerals known to date have been described from deposits in sedimentary rocks, and some were described from the oxidized zone of base metal deposits. Over half of the more than forty vanadium minerals known on the Colorado Plateau (Table II) were first found and named from there.

Although the total number of vanadium minerals found on the Colorado Plateau is large, many of these minerals are very rare and only the more important minerals will be discussed here. Vanadium forms many hydrated oxide minerals and it combines with many other elements to form simple as well as complex vanadates. It also is common in silicate minerals such as roscoelite, hydrous mica, and chlorite. Very

rarely on the Plateau does vanadium occur in a phosphate mineral. The principal mineral groups from the commercial point of view are the silicates, vanadates and oxides. The early miners and mill-men distinguished and gave names to two types of ore — "roscoelite ore" and "carnotite ore". The names are not strictly correct and they are now somewhat out of date but they serve to emphasize the difference between ore containing chiefly vanadium silicate minerals, and ore containing chiefly the oxide–vanadate groups of minerals.

TABLE II

VANADIUM MINERALS FOUND ON THE COLORADO PLATEAU

Oxides

Montroseite, VO(OH)
Häggite, $V_2O_2(OH)_3$
Paramontroseite, VO_2
Doloresite, $3\ V_2O_4 \cdot 4H_2O$
Duttonite, $VO(OH)_2$
Navajoite, $V_2O_5 \cdot 3\ H_2O$

Phosphates

Sincosite, $CaV_2O_2(PO_4)_2 \cdot 5\ H_2O$

Vanadite

Simplotite, $CaV_4O_9 \cdot 5\ H_2O$

Vanadyl vanadates

Melanovanadite, $2\ CaO \cdot 2\ V_2O_4 \cdot 3\ V_2O_5 \cdot H_2O(?)$
Sherwoodite, $Ca_3V_8O_{22} \cdot 15\ H_2O$
Fernandinite, $CaO \cdot V_2O_4 \cdot 5\ V_2O_5 \cdot 14\ H_2O$
Corvusite, $V_2O_4 \cdot 6\ V_2O_5 \cdot n\ H_2O$
Corvusite-like mineral, $V_2O_4 \cdot 5\ V_2O_5 \cdot 12\ H_2O$
New calcium vanadyl vanadate
New sodium calcium vanadyl vanadate
New potassium iron vanadyl vanadate

Silicates

Roscoelite, $K(Al, V)_2(Al,Si_3)O_{10}(OH,F)_2$
Vanadium-bearing hydrous mica
Vanadium-bearing chlorite

Vanadates

Descloizite, (Zn, Cu)Pb$(VO_4)(OH)$
Santafeite, $Na_2O \cdot 3\ MnO_2 \cdot 6(Mn,Ca,Sr)O.3(V, As)_2O_5 \cdot 8\ H_2O$

Tangeite, $CuCa(VO_4)(OH)$
Vésigniéite, $Cu_3Ba(VO_4)_2(OH)_2$
Volborthite, $Cu_3(VO_4)_2 \cdot 3\ H_2O$
Vanadinite, $Pb_5(VO_4)_3Cl$
Carnotite, $K_2(UO_2)_2V_2O_8 \cdot 3\ H_2O$
Tyuyamunite, $Ca(UO_2)_2V_2O_8 \cdot 5–8\frac{1}{2}\ H_2O$
Metatyuyamunite, $Ca(UO_2)_2V_2O_8 \cdot 3–5\ H_2O$
Fervanite, $Fe_2(VO_4)_2 \cdot 2\frac{1}{2}\ H_2O$
Steigerite, $Al_2(VO_4)_2 \cdot 6\frac{1}{2}\ H_2O$
Brackebuschite, $Pb_4MnFe(VO_4)_4 \cdot 2\ H_2O$
Delrioite, $SrO \cdot CaO \cdot V_2O_5 \cdot 3\ H_2O$
Rossite, $CaV_2O_6 \cdot 4\ H_2O$
Metarossite, $CaV_2O_6 \cdot 2\ H_2O$
Pascoite, $Ca_3V_{10}O_{28} \cdot 16\ H_2O$
Hummerite, $K_2Mg_2V_{10}O_{28} \cdot 16\ H_2O$
New sodium decavanadate
Uvanite, $2\ UO_3 \cdot 3\ V_2O_5 \cdot 15\ H_2O(?)$
Rauvite, $CaO \cdot 2\ UO_2 \cdot 6\ V_2O_5 \cdot 20\ H_2O(?)$
Hewettite, $CaV_6O_{16} \cdot 9\ H_2O$
Metahewettite, $CaV_6O_{16} \cdot 3\ H_2O$
Barnesite, $Na_2V_6O_{16} \cdot 3\ H_2O$

Sandstone containing vanadium silicate ore ranges from light tan or gray to medium brown or dark gray depending on the content of vanadium. This type constitutes virtually all of the ore at the large mine near Rifle, Colorado, and a large bulk of the vanadium ore that was mined in near-surface deposits farther west in the Uravan mineral belt[11] in Colorado and in Utah, Arizona, and New Mexico. The vanadium-bearing mica, clay, and chlorite minerals are very fine-grained aggregates between the quartz grains, or films coating the quartz, or clay balls which have been converted to vanadium clay. Chemical investigations by FOSTER[6] and X-ray diffraction studies by HATHAWAY[7] have shown that much of the vanadium silicate is a mixed-layer mica-montmorillonite type of clay. Roscoelite is present in small quantity except at Placerville, Colorado, where it seems to predominate. Chlorite is common in many of the Uravan district deposits. FOSTER[6] has shown that 4-valent vanadium is present

in all of the mineralogical phases making up the mineralized clays. She found that the most significant difference between mineralized and unmineralized clay is the progressive decrease in SiO_2 and Al_2O_3 with increase in V_2O_4 content. Vanadium replaces aluminum ion for ion as an octahedral cation in the clay structure. Substitution of 4-valent vanadium for 3-valent aluminum causes an equivalent decrease in octahedral charge which is compensated for by increased replacement of silicon by aluminum in the tetrahedral position. She concludes that vanadium entered the structures of the clays in the 4-valent state, and not in the 3-valent state as in true roscoelite. These clay and mica minerals are not easily altered by oxidation and are much more stable than the low-valent vanadium oxides and vanadates.

The term "carnotite ore" was used by the early miners to distinguish the uranium–vanadium ore from the vanadium ore. Disseminated yellow specks of carnotite in the sandstone indicated the presence of uranium. Before World War II, carnotite and so-called roscoelite were the dominant minerals[12] and other vanadium and uranium minerals were considered too rare to be of much importance. Until about 1948 almost all of the production was from oxidized (yellow) ores in very shallow mines ranging from small open pits to depths in mines that were rarely as much as 100 feet below the surface. In the late 1940's and early 1950's deeper mining began to penetrate black unoxidized ores in water-saturated rocks[13]. Within a few years it became apparent that the carnotite ores have been derived by progressive oxidation of primary (unoxidized) black ores that contain low-valent uranium and vanadium oxides and vanadium silicates. The odd-ball minerals of the early 40's began to fit into a consistent picture of an oxidation sequence, and more new vanadium minerals than the total number previously known on the Plateau were discovered. Thus, the mineralogy of so-called carnotite ore has become quite complex[4,8].

In 1950 the recently discovered black vanadium ore was studied in several mines of the Uravan district and it was found to contain a trivalent vanadium oxide, VO(OH), to which the name montroseite was given. This is considered one of the primary vanadium minerals. Another mineral which probably is also primary is häggite, $V_2O_3 \cdot V_2O_4 \cdot 3\ H_2O$ or $H_6V_4O_{10}$[14]. These two are both abundant in unoxidized vanadium ores. As oxidation begins doloresite, $3\ V_2O_4 \cdot 4\ H_2O$ or $V_3O_4(OH)_4$, and paramontroseite are common. By solid state oxidation paramontroseite VO_2 is derived from montroseite. At this stage well-crystallized but rare minerals, are duttonite $VO(OH)_2$ and simplotite $CaV_4O_9 \cdot 5\ H_2O$. These are limited to slightly more alkaline environments than the average ore. The bulk of the V^{4+} minerals oxidize in a weakly acid environment and form the V^{4+} and $^{5+}$ minerals of the corvusite group. These are complex, poorly-crystallized vanadyl vanadates with varying ratios of V^{4+} to V^{5+} and they are still not clearly defined.

Although many vanadates were known before the recent work several new ones were found. As mines in blue–black ore were opened moisture from the ore evaporated on the mine walls leaving bright orange coatings. Study of this revealed a new mineral hummerite with the composition $K_2Mg_2V_{10}O_{28} \cdot 16\ H_2O$[15]. The true formula of the orange calcium vanadate known as pascoite was then found to be $Ca_3V_{10}O_{28} \cdot 16\ H_2O$. EVANS recognized the importance of the soluble polyvanadate ion $V_{10}O_{28}^{-6}$ in the oxidation and migration of vanadium.

Quantitatively the most important vanadates are hewettite, $CaV_6O_{16} \cdot 9\ H_2O$, and carnotite, $K_2(UO_2)_2V_2O_8 \cdot 3\ H_2O$. The least soluble vanadium complex in the oxidized

environment is carnotite and its analogues (Ca, Ba, and Cu). The crystal structure of carnotite has been found by recent work to have the structural and chemical properties of a metavanadate. It contains $V_2O_8^{-6}$ groups with vanadium in five-fold co-ordination[16].

As the mineralogic and geologic background of vanadium in the Colorado Plateau grew, GARRELS AND EVANS[4,17,18] related the geochemical properties of vanadium with those that can be predicted from thermodynamic studies.

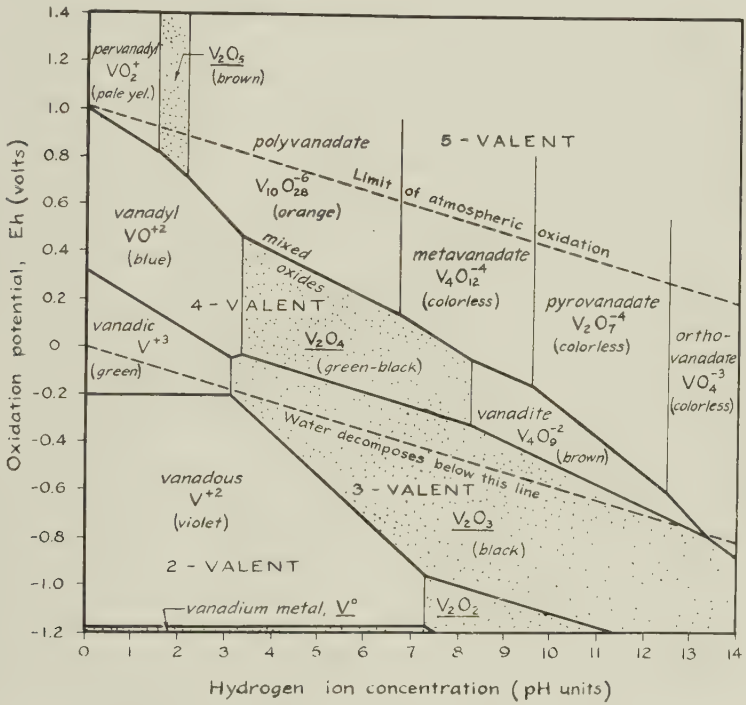

Fig. 1. Oxidation potential–pH phase diagram for vanadium in aqueous solutions. Stippled fields represent solids (solubility of V <0.01 mol/l). Phases may be hydrated or hydrogenated to an unknown degree[4].

They used all available chemical and thermodynamic data to develop an oxidation potential–pH phase diagram for vanadium in aqueous solutions (Fig. 1). The stippled areas represent fields of stability of solids (defined as fields where the solubility of the solid is less than about 0.01 mole per liter of the major vanadium species in equilibrium). The two sloping dashed lines show the normal limits of redox potential in nature and only 3-, 4-, and 5-valent vanadium occur above the lower limit. The pH range in nature is generally mildly acid to mildly alkaline with values rarely as low as pH 2 or as high as 10 or 11. Therefore only the middle portion of the diagram is important in natural environments. EVANS also considered the hydrated mineral phases and showed the positions of some of the mineral species on the central portion of an E_h–pH diagram (Fig. 2). Arrows indicate probable alteration sequences such as montroseite-paramontroseite-corvusite-hewettite under acid conditions and montroseite-

doloresite–duttonite–melanovanadite–rossite under alkaline conditions. Data and interpretation of new phases in the montroseite–doloresite area were given in a recent paper by EVANS AND MROSE[14] in which Fig. 11 shows more details in a portion of the E_h–pH diagram. The theoretical considerations agree with field observations of the mineral assemblages and alteration sequences. One of the important controls of pH as oxidation progresses in the ores near the surface of the ground is the relative abundance of pyrite and calcite.

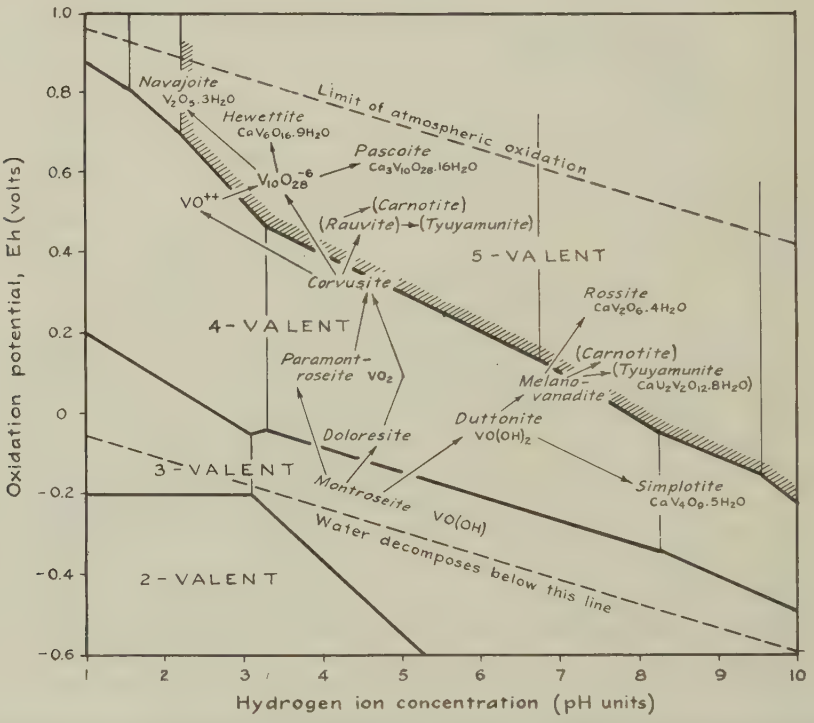

Fig. 2. Portion of the E_h -pH phase diagram of Fig. 1, showing positions of various mineral species and probable alteration sequences[4].

ORIGIN OF THE COLORADO PLATEAU VANADIUM DEPOSITS

Geologists are always interested in trying to determine the origin of ore deposits partly because of curiosity but largely to know the habits of the ore, classify the deposits, and learn how to find more ore. For the Colorado Plateau vanadium deposits we want to know: (1) when the vanadium was deposited in the sandstone — whether at the same time as the sand and clay were laid down or after the sediments were consolidated; (2) how the vanadium was transported, what caused it to precipitate, and whether vanadium is still migrating in the ground water; and (3) what was the ultimate source of the vanadium. Through the joint effort of many people some of these questions have been answered but there is still considerable controversy on certain aspects of the origin.

The habits of the minerals as replacements of coalified logs, fillings in pore spaces,

or oriented growths around quartz grains indicate the ore was formed after the sandstone was deposited (see plates 1, 2, 6, 7 and 8 in GARRELS AND LARSEN[2]). Lead–uranium determinations[19] indicate that the uranium was deposited millions of years after the sandstone was formed. Study of the oxidation sequence of the minerals indicates that carnotite and the other high-valent minerals have been derived by recent oxidation of a primary low-valent suite of minerals, as erosion of the land surface allowed access of oxygen to the deposits[5]. The low-valent minerals apparently were deposited by reduction from solutions migrating through the sandstone. Considerable thought has been devoted to the chemical nature of the solutions that transported the metals. The best explanation so far seems to be that 4-valent vanadium as the vanadite ion and 6-valent uranium as the uranyl ion were transported in a moderately reducing, mildly alkaline solution at temperatures not significantly above the geothermal gradient[20]. This is reasonable considering the solution chemistry of uranium and vanadium and the nature of the sandstone host rocks. The fact that some silica has been dissolved from quartz grains and redistributed and that calcite is the common cement of the sandstone is in accord with alkaline carbonate solutions rather than acid solutions. If the vanadium were 5-valent instead of 4-valent it would precipitate the 6-valent uranium as carnotite. Only if the solutions are moderately reducing so that the vanadium is 4-valent could vanadium be transported with the uranyl ion. In the primary suite of minerals vanadium in montroseite is 3-valent, and in the silicates it is 3-valent in roscoelite and 4-valent in chlorite and hydrous micas. The primary uranium minerals uraninite and coffinite contain chiefly 4-valent uranium, although when formed at low temperature they generally contain some U^{6+}. These low-valent minerals were precipitated by reduction in the environment of carbonaceous material or H_2S gas, probably by change in pH as well as E_h.

The questions of where the alkaline carbonate solution picked up the vanadium and of the ultimate source of the vanadium are much more speculative and controversial. The vanadium may not have come from the same place as the uranium (many geologists would say it probably did not come from the same place).

Possibilities for the source of vanadium include the sandstone host rocks themselves, petroliferous rocks, and hydrothermal solutions from magmatic sources. This writer favors either or both of the first two possibilities. FISCHER AND STEWART[21] have reviewed the distribution of all of the vanadium, uranium, and copper deposits in the Colorado Plateau and concluded that vanadium deposits are chiefly in second-cycle sandstone. The implication may be that vanadium could be released from resistant minerals in sandstone during the second weathering cycle.

BOWERS AND SHAWE[22] studied the distribution of heavy minerals in unaltered sandstone and in large areas of slightly altered sandstone that include and surround the vanadiferous uranium deposits. Magnetite and ilmenite are common in unaltered rock but hematite and leucoxene or pyrite and anatase take their place in altered rocks. Traces of vanadium would be released during this alteration and since the total volume of altered rock is great the total vanadium would be significant.

The possibility of a source of vanadium from petroliferous material is of interest because the vanadiferous ores of the Uravan mineral belt in Colorado are in sandstone overlying rocks of the Paradox basin. To the south and southwest of Uravan where the rocks are only slightly deformed, petroleum is produced from these basin rocks. In the Uravan belt the Paradox basin rocks are highly deformed by the intrusion of

salt anticlines that have pushed up through all the sediments and only traces of petroleum remain. A significant source of vanadium may have been available from petroleum escaping from these deformed source beds.

In contrast, the uranium is thought by many geologists to have been leached from thick deposits of volcanic sediments interbedded with the sandstones and shales of the Plateau; and some geologists maintain that hydrothermal fluids brought both the uranium and vanadium up through fractures from deep under the Plateau.

REFERENCES

1 R. P. Fischer, Uranium–vanadium–copper deposits on the Colorado Plateau, in *Contributions to the Geology of Uranium and Thorium*, U.S. Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy, (1956), pp. 143–154.

2 R. M. Garrels and E. S. Larsen (compilers), Geochemistry and mineralogy of the Colorado Plateau uranium ores, *U.S. Geol. Survey Profess. Paper 320*, (1959).

3 R. P. Fischer, Vanadium and uranium in rocks and ore deposits, in Garrels and Larsen, *U.S. Geol. Survey Profess. Paper 320*, (1959), pp. 219–230.

4 H. T. Evans, Jr., The crystal chemistry and mineralogy of vanadium, in Garrels and Larsen, *U.S. Geol. Survey Profess. Paper 320*, (1959), pp. 91–102.

5 R. M. Garrels and C. L. Christ, Behavior of uranium minerals during oxidation, in Garrels and Larsen, *U.S. Geol. Survey Profess. Paper 320*, (1959), pp. 81–89.

6 M. D. Foster, Chemical study of the mineralized clays, in Garrels and Larsen, *U.S. Geol. Survey Profess. Paper 320*, (1959), pp. 121–132.

7 J. C. Hathaway, Mixed-layer structures in vanadium clays, in Garrels and Larsen, *U.S. Geol. Survey Profess. Paper 320*, (1959), pp. 133–138.

8 A. D. Weeks, R. G. Coleman and M. E. Thompson, Summary of the ore mineralogy, in Garrels and Larsen, *U.S. Geol. Survey Profess. Paper 320*, (1959), pp. 65–80.

9 B. Mason, *Principles of Geochemistry*, 2nd edn., John Wiley and Sons, New York, 1958, p. 44.

10 K. Rankama and T. G. Sahama, *Geochemistry*, Univ. of Chicago Press, Chicago, 1950, p. 594.

11 R. P. Fischer and L. S. Hilpert, Geology of the Uravan mineral belt, *U.S. Geol. Survey Bull. 988-A*, (1952), pp. 1–13.

12 R. P. Fischer, Vanadium deposits of Colorado and Utah, a preliminary report, *U.S. Geol. Survey Bull. 936-P*, (1942), pp. 363–394.

13 A. D. Weeks, Mineralogy and oxidation of the Colorado Plateau uranium ores, in *Contributions to the Geology of Uranium and Thorium*, U. S. Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy, (1956), pp. 187–193.

14 H. T. Evans, Jr. and M. E. Mrose, *Am. Mineralogist*, 45 (1960) 1144.

15 A. D. Weeks and M. E. Thompson, Identification and occurrence of uranium and vanadium minerals from the Colorado Plateaus, *U.S. Geol. Survey Bull. 1009-B*, (1954), p. 13–62.

16 D. E. Appleman and H. T. Evans, Jr., *Acta Cryst.*, 10 (1958) 765.

17 R. M. Garrels, *Am. Mineralogist*, 38 (1953) 1251.

18 H. T. Evans, Jr. and R. M. Garrels, *Geochim. et Cosmochim. Acta*, 15 (1958) 131.

19 L. R. Stieff, T. W. Stern and R. G. Milkey, A preliminary determination of the age of some uranium ores of the Colorado Plateaus by the lead-uranium method, *U.S. Geol. Survey Circ. 271*, (1953).

20 R. M. Garrels, P. B. Hostetler, C. L. Christ and A. D. Weeks, *Bull. Geol. Soc. Am.*, 68 (1957) 1732.

21 R. P. Fischer and J. H. Stewart, Distribution and lithologic characteristics of sandstone beds that contain deposits of copper, vanadium, and uranium, *U.S. Geol. Survey Profess. Paper 400-B*, (1960), pp. B-42–B-44.

22 H. E. Bowers and D. R. Shawe, private communication, (1960).

CONSOLIDATION AND FABRICATION OF VANADIUM*

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SUMMARY

This paper describes the semi-commercial consolidation and fabrication of calcium-reduced vanadium metal into wrought forms, currently being ordered to permit property studies and evaluation for specific applications. Ingots up to 6 in. diameter are melted by the consumable electrode vacuum arc process. Hot rolling with commercial facilities requires heating in inert atmosphere. Cold working is carried out successfully provided the surface contamination resulting from the hot working operation is completely removed. Warm extrusion of ingots successfully avoids the hot working step. Machining and welding operations are feasible.

INTRODUCTION

Ductile vanadium is an interesting new metal with good high temperature strength, excellent corrosion resistance and with properties which qualify it for atomic reactor use. It is produced from a domestic ore which is in plentiful supply. There has as yet been too little work done for any commercial applications to have been developed, although many investigations are in progress to determine its suitability in a number of fields.

Ores of vanadium are found as economic mineral deposits in Peru, Northern Rhodesia, Southwest Africa and, most importantly, on the Colorado Plateau. Carnotite, found in our western states, is at present the principal ore from which vanadium is extracted. It contains about 1% vanadium as well as about $\frac{1}{2}$% uranium. "Red cake", approximated by the formula $Na_2H_2V_6O_{17}$ (sodium hexavanadate), is obtained from the ore by a solution-precipitation process. This product is further purified by another process, similar in nature, resulting in a pure oxide. There has been no serious shortage of vanadium for many years even though it is widely used, as ferrovanadium, in the production of many tool, forging, and constructional steels.

Although vanadium has been used as an alloying element for steels and irons since the beginning of the century, it was not realized until about ten years ago that it is a ductile metal when in sufficiently pure form. To arrive at the required purity, calcium reduction of the oxide in a pressure vessel was found necessary. Although this is not the only process known today, it is the one in greatest use and it is satisfactory for current demands.

Purified vanadium oxide, calcium metal, and iodine are charged into a thick-walled steel vessel, taking care to exclude all moisture. The reaction between the oxide and the reducer is initiated by the application of heat. A regulus or button of metal quickly

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forms at the bottom of the vessel below the resulting slag. The buttons we produce are less than fifty pounds in weight and have the following typical composition: V, 99.8%; Fe, 0.03%; C, 0.04%; N, 0.03%; O, 0.08%; H, 0.005%.

MELTING

Remelting of the button has been found convenient to put the metal in ingot form for further processing and to lower the oxygen content somewhat, particularly where some contamination has occurred during the fabrication of electrodes. The consumable electrode, vacuum arc process is the most convenient one for melting vanadium,

Fig. 1. On the left, a portion of an electrode for consumable arc melting prepared by compacting crushed material; on the right, a welded joint in an electrode produced of strips cut from the as-reduced regulus.

primarily because most refractories will not contain molten vanadium and at best cause serious contamination of the metal. We have used two methods for making electrodes: the as-reduced button can be sawed into strips which are then welded together end to end to a convenient length for melting, or the button can be crushed to a size below $\frac{1}{4}$ in. and the particles compressed in a suitable press to form a

convenient shape. These two forms of electrodes are illustrated in Fig. 1. Neither method is completely satisfactory. The sawed strips are often not flat and have rounded ends which are not ideal for welding. Compressing the crushed metal requires considerable pressure to avoid loose corners which cause difficulty in welding. It is well to remove the surface oxidation encountered during the welding of either the strips or the compacts by mechanical or chemical means before placing the electrodes in the furnace.

The melting operation is started by arcing at full power on a small amount of crushed metal placed on the bottom of a copper crucible. Optimum current and voltage settings are determined by trial, using a low enough current to avoid excessive splashing yet high enough to prevent glow discharge for each electrode and ingot combination. We have found the current–voltage combinations shown in Table I to be optimum.

TABLE I

Mold size (in.)	*Current (A)*	*Voltage (V)*
2	1200	22
4	2200	28–30
6	4000	30

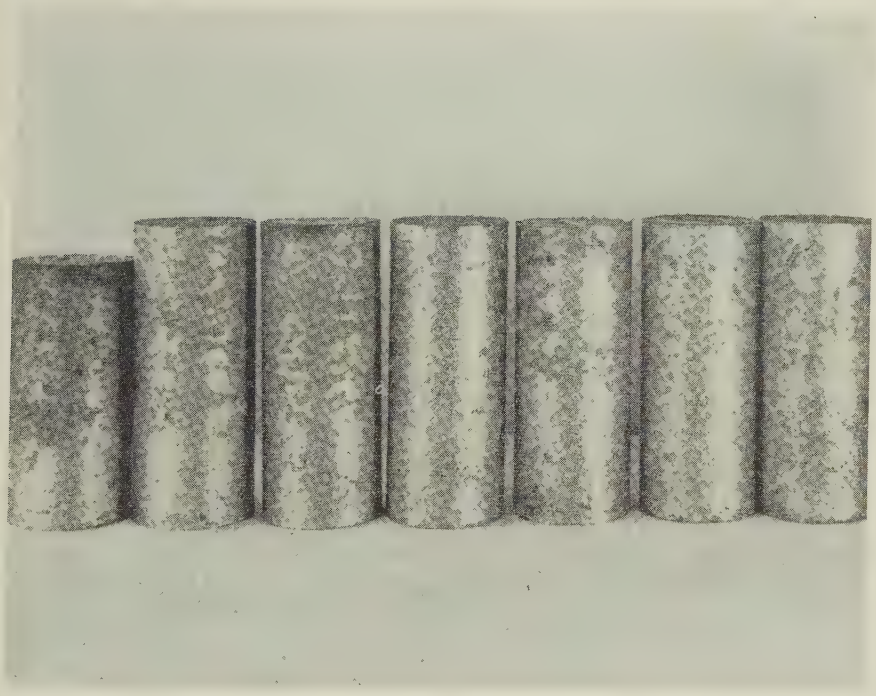

Fig. 2. Some 4 in. diameter ingots of vanadium metal.

We have found that the pressure in the furnace during the first melt varies with the purity of the metal and the cleanliness of the joints, but is often high, up to 1 mm. During the second melt, on the other hand, the pressure is usually below 10 μ. In our

experience, hot topping procedures have not proved to be beneficial, that is, for ingots 6 in. diameter and smaller. Stirring during melting does appear to help the surface quality of the ingot.

Melting vanadium in a vacuum arc furnace does lower the oxygen content. For example, an electrode fabricated from a button containing 0.10% oxygen might be found to contain 0.08% oxygen after the first melt and 0.06% oxygen after the second melt. Typical ingots are shown in Fig. 2.

An electron beam furnace removes considerably more oxygen from vanadium than a vacuum arc furnace. We have had several ingots produced by this process and have found oxygen contents as low as 0.004% in metal which contained approximately 0.10% oxygen in the button form. The advantage of such a low oxygen content is not yet obvious.

HOT WORKING

The hot working of vanadium ingots can be accomplished easily if the metal is well protected during heating. We have found no brittle ranges to be avoided. The starting temperature is determined by the length of the hot working operation and by the desired finishing temperature, with the important consideration that reheating is to be avoided if at all possible. Starting temperatures as high as 2300°F have been found

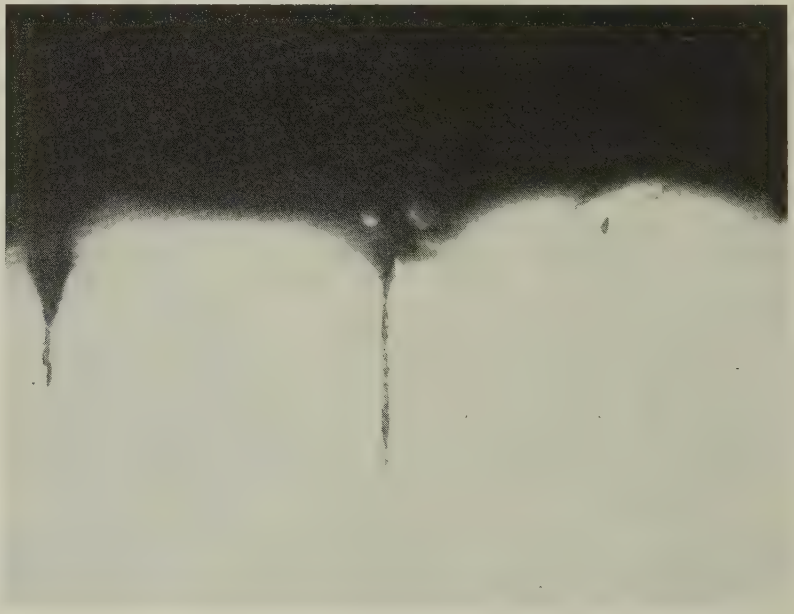

Fig. 3. A cross section at the surface of a vanadium bar after heating to 2100°F for 30 min. (×500)

to be practical while finishing temperatures are limited by the stiffening of the metal as it cools and by the relatively high recrystallization temperature (1500°F to 1800°F approximately). Finishing in the range of 1400° to 1600°F is typical.

Oxygen and nitrogen from the air penetrate the surface of vanadium metal quite

rapidly at elevated temperatures. Vanadium oxide melts at temperatures above 1250°F and flows off surfaces that are not horizontal. The contamination of the surface appears not to be uniform but to penetrate as small fingers perpendicular to the surface. This action hardens and embrittles the metal while the fingers act as stress raisers which are very effective after the metal has cooled and apparently can even initiate cracking during hot working. A photomicrograph taken perpendicular to the surface of a hot rolled bar is shown in Fig. 3.

Considerable effort has been made to overcome the contamination problem during heating. Nickel and copper plating peels off during heating. Immersion in molten lead and salts permits some contamination. Coatings of paste or powders such as borax have been found ineffective. Heating in chambers filled with inert gas appears to be a reasonable compromise since it is practicable in most shops. Lack of gas-tight closures on such chambers appears to prevent full protection, but with short heating times the method can be used. As an example, Fig. 4 shows the hardness of the sample from the surface inward after heating in a retort continuously flushed with argon. Reheating, even in argon, appears to drive the oxygen inward from the surface, usually resulting in excessive brittleness.

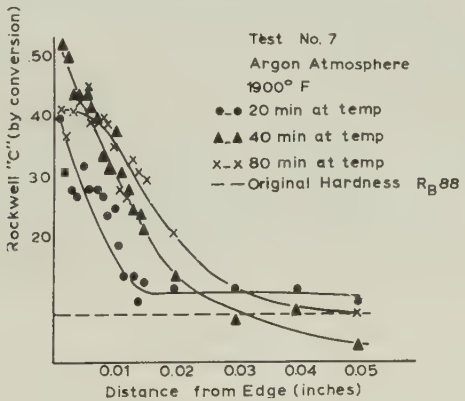

Fig. 4. Variation in hardness of a cross section of a vanadium specimen after heating in the manner indicated.

We believe that vanadium ingots, that is the 6 in. and under size we have been working with, can be hot worked rapidly if the surface is not overly contaminated during heating. However since this is usually an unknown factor, some caution has appeared advisable, using procedures common to alloy steels.

Hot rolled vanadium sections can be straightened if they are warm, that is in the range between 700° and 800°F. If this operation is attempted after the bars are cold, cracking generally results. Reheating to the above range for straightening has been successful.

Dye penetrant and ultrasonic inspection methods are useful, the former for detecting small surface breaks and the latter for investigating the soundness of ingots and wrought products.

COLD WORKING

Vanadium already has an excellent reputation for its ability to be cold worked without excessive hardening. The key to successful cold working appears to be the achievement of uncontaminated surfaces on the piece to be rolled. We have found it necessary to machine all hot worked surfaces, removing 0.020–0.040 in. from each surface. Hardness appears to be a reasonable criterion of clean surfaces. There is no good reason to think that grinding would not be satisfactory, although precautions must be taken to avoid overheating and consequent cracking. The extreme hardness of the contaminated surface of hot worked bars, as high as Rockwell C 60, requires that precautions be taken.

Hot rolled slabs $\frac{3}{4}$ in. in thickness by 6 in. in width can be cold worked readily to thin strip. It is not unusual to be able to reduce from $\frac{3}{4}$ in. to less than 0.010 in. without annealing. Some bars, however, appear to harden and begin to crack at intermediate sizes. Annealing is then required. It seems probable that the ability of vanadium to be cold worked is reduced by contamination with the interstitial elements oxygen and nitrogen. We have not established the precise tolerance of the metal for these elements with respect to cold rolling. A typical practice in producing cold rolled strip has been to start on a two-high mill having 18 in. diameter rolls, making reductions of 0.025 in. per pass. At a thickness of 0.200 in. the material is transferred to a four-high mill having 5 in. diameter working rolls. Again reductions of 0.025 in. are taken until the desired thickness is reached.

The annealing of cold rolled vanadium has been carried out at 1650°F in vacuum. Only a short time is required, 5–10 min at temperature. Presumably annealing in a completely inert atmosphere would be satisfactory. Reductions up to 75% with no annealing are the rule and more than 99% is not unusual.

Wire drawing has been carried out successfully. A rod size of $\frac{3}{8}$ in. diameter is suitable. Copper plating of the rod aids the operation considerably. Carbide drawing dies for the larger sizes and diamond dies for the smaller sizes have been used. Reduction in relatively small steps has been the practice, approximately 10% per pass. Wire as small as 0.010 in. has been made. Many of the common practices used for other metals have not been successful in drawing vanadium wire.

EXTRUSION

Extrusion of vanadium at temperatures below 1000°F has proved to be one of the easiest ways of fabricating. Tube blanks 2 in. o.d. by $\frac{1}{4}$ in. wall have been extruded from hot rolled and turned bars as well as from turned ingots. Extrusion of ingots greatly simplified fabrication by avoiding the troublesome heating operations and the laborious conditioning of the hot worked product. Under the right circumstances, it appears to be more economical to warm extrude ingots and to cold roll or cold draw the product, omitting the hot working step altogether. For quantity production of large sizes, such a process, of course, may be impractical.

MACHINING

The machining of vanadium is somewhat comparable to that of the more difficult stainless steels once the hard, contaminated surface is removed. Galling of the tool is the common difficulty. Low speeds with light to moderate feed is the best practice, although very light finishing cuts at higher speeds are practicable. The photograph

in Fig. 5 shows a 0.020 in. cut being made on a 4 in. ingot at 78 s.f.m. In using multi-toothed tools, such as saws and milling cutters, considerable power is used and slow speeds with light feed are necessary to avoid breakdown. A deep cut at very slow speeds is the common way of contending with the hard surface on hot worked products. Vanadium can be ground satisfactorily if overheating is avoided.

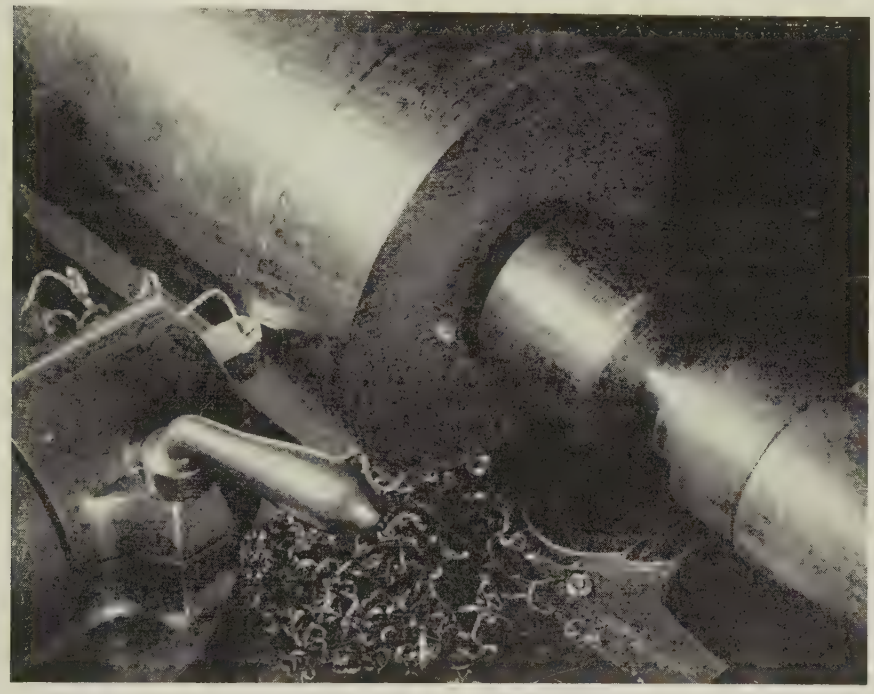

Fig. 5. Machining of a vanadium ingot; a 0.020 in. cut being made at 78 s.f.m.

WELDING

Welding of vanadium is not difficult if proper precautions are taken to avoid contamination of the molten metal and the adjacent heated zones. The ductility of welds appears to be determined by the degree to which contamination is avoided. Inert gas metal-arc welding can be used for small, short welds. For larger continuous welds, additional precaution appears to be called for, such as the use of additional jets of inert gas or welding in a gas flushed container. Of course, welding inside a gas-tight container filled with purified inert gas is the surest method.

In summary, vanadium metal products can be produced by hot working, cold working, welding, and machining. We have not investigated the casting of vanadium to shape. Demand for the product has been small, requirements have been largely for sample lots. This has not been conducive to the establishment of the most efficient and economical production methods. Maintaining purity during the fabricating operations has been the biggest fabricating difficulty. Ease of cold working has been the biggest asset in this respect. We are confident that when the demand arises, efficient and economical methods will be found for fabricating any desired size or shape. This will, of course, be reflected in the selling price.

CORROSION PROPERTIES OF HIGH-PURITY VANADIUM*

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SUMMARY

Vanadium is relatively resistant to corrosion in phosphoric, sulfuric, and hydrochloric acids at 35° and 60°C, but corrodes rapidly in nitric acid solutions. Vanadium is almost inert in 10% formic, acetic, lactic, tartaric, and citric acids and is quite resistant to corrosion in 9% oxalic acid. Vanadium is resistant to corrosion in substitute ocean water, 3% sodium chloride solution, tap water, and 10% sodium hydroxide solution but not in 20% ferric chloride or 5% mercuric chloride solutions.

Vanadium is protected by contact with magnesium, aluminium, or steel SAE 4130. Vanadium and stainless steel are usually not affected by contact with each other. Contact with vanadium may greatly reduce the corrosion rate of titanium in sulfuric acid solutions.

INTRODUCTION

Several companies are now producing small amounts of pure vanadium. This material is ductile and has other physical and mechanical properties desirable in a structural metal. Lower production costs and the accumulation of information about its properties will further the development of vanadium as a useful metal.

The Federal Bureau of Mines is investigating the properties of vanadium and some of its alloys. Studies of the corrosion properties of these metals are part of the program. Some data have been published[1] and show that at 35°C vanadium is resistant to corrosion in substitute ocean water and in rather concentrated sulfuric and hydrochloric acid solutions. It corrodes rapidly in nitric acid. The results of galvanic couple experiments in substitute ocean water with a flow of air indicate that the corrosion characteristics of vanadium and stainless steel are not affected by contact between the two metals. Vanadium corrodes a little faster as a result of contact with copper, and the corrosion of copper is eliminated. In the vanadium–SAE 4130 steel couple, the corrosion of vanadium is almost stopped, and corrosion of steel is doubled. When coupled with magnesium, the corrosion of vanadium is eliminated and that of magnesium is greatly increased. The corrosion of vanadium becomes negligible as a result of contact with aluminum, and aluminum corrodes a little faster.

This paper includes the results of additional work on the chemical and galvanic corrosion properties of high-purity vanadium in various corrodents at 35° and 60°C.

EXPERIMENTAL

Chemical corrosion experiments were conducted at 35° and 60°C and lasted 6 or 30

* Paper presented at the Symposium on Vanadium of the Electrothermics and Metallurgy Division of the Electrochemical Society, May 2, 1960, Chicago, Illinois.

days; galvanic corrosion experiments were done at 35°C and lasted 15 days. Pure chemicals, grade A helium (99.9+% pure), and standard commercial metals were used. The substitute ocean water used in this work was prepared according to a formula developed by the American Society for Testing Materials[2] and had the following composition (g/l): NaCl, 24.53; $MgCl_2 \cdot 6\ H_2O$, 11.11; Na_2SO_4, 4.09; $CaCl_2$, 1.16; KCl, 0.695; $NaHCO_3$, 0.201; KBr, 0.101; H_3BO_3, 0.027; $SrCl_2 \cdot 6\ H_2O$, 0.42; NaF, 0.003. Tap water (College Park, Md.) used for these tests had the following analysis, according to information supplied by the Washington Suburban Sanitary Commission, Hyattsville, Md. (p.p.m.): hardness (total), 31–44; alkalinity (total), 15–30; alkalinity CO_3, 3–6, alkalinity HCO_3, 10–24; SiO_2, 0.2–2.8; Ca, 7–19; Mg, 0.2–3; SO_4, 7–13; fluoride, 0.7–1.0; Fe (total), 0.0; Fe_2O_3 and Al_2O_3, 0–5; Cl_2 (starch KI), 1.0; Mn, 0.0; NH_3 (free), 0.0; solids, 50–100; chlorides, 2–7.5. In addition, the content of dissolved oxygen was 87–100% saturated, and the pH was 8.7.

Vanadium sheet used in these experiments was purchased from two commercial suppliers or prepared in Bureau of Mines laboratories. Commercial vanadium was always cold-rolled to finished sheet. Unannealed Bureau of Mines vanadium was 70% cold-rolled and had R_B hardnesses of 77–88; other strips were annealed 1 h at 900°C in a vacuum of $5 \cdot 10^{-5}$ mm Hg and had hardnesses of 62–70. Impurity contents of vanadium from the several sources are given in Table I.

TABLE I

ANALYSIS OF VANADIUM (%)

Source	*C*	O_2	H_2	N_2	*Fe*	*Cr*
Commercial supplier 1	0.032	0.06–0.13	0.001–0.00019	0.033 0.042	0.026	0.011
Commercial supplier 2	0.046–0.100	0.034–0.170	0.0022–0.0031	0.035–0.070	0.019–0.032	—
Bureau of Mines	—	0.062–0.107	—	0.004–0.03	0.21–0.48	0.02–0.06

Vanadium specimens cut from commercial sheet for chemical corrosion experiments were 1 by 1 by 0.06 in.; those cut from Bureau of Mines sheet were 2 by 0.5 by 0.06 in. Galvanic couple specimens were 1/4 in. wide and 6 in. long. All specimens were cut and machined to 0.003–0.005 in. oversize and given a preliminary polish on a mechanical sander using 120-mesh abrasive cloth. Just before immersion, the specimens were handpolished with dry 3/0 emery cloth, rubbed with wet pumice, rinsed with water, dried, washed with carbon tetrachloride, and weighed. At the end of the experiment, adherent corrosion products were removed by scraping the specimen with a rubber stopper. A chemical reagent was employed when necessary.

Experiments were conducted with a constant flow of helium or air through the corrodent. Before entering the corrosion apparatus, the gases were passed through water to saturate them with water vapor at room temperature; air was also bubbled through 3% sodium hydroxide solution to remove carbon dioxide. After this preliminary treatment, the helium or air was passed through the corrodent contained in one of the sets of apparatus in Figs. 1A, 1B, and 2. The apparatus in Figs. 1B and 2 consisted of a sealed bottle with a gas inlet and outlet and two water vessels. The incoming air or helium was passed through one water vessel to saturate the gas with

water vapor at 35°C thus avoiding evaporation in the specimen vessel, and the outgoing gas was passed through the other water vessel which served as a trap.

The gases were passed through the solution for about 1 h before immersion of metal specimens and continuously throughout the experiment. Rates of flow, measured with rotameters, were approximately 250 ml/min for both helium and air.

Chemical corrosion experiments were conducted with the specimens completely immersed in 750 ml of corrodent contained in the apparatus shown in Fig. 1. Two specimens were placed in each corrosion vessel. The apparatus used in substitute

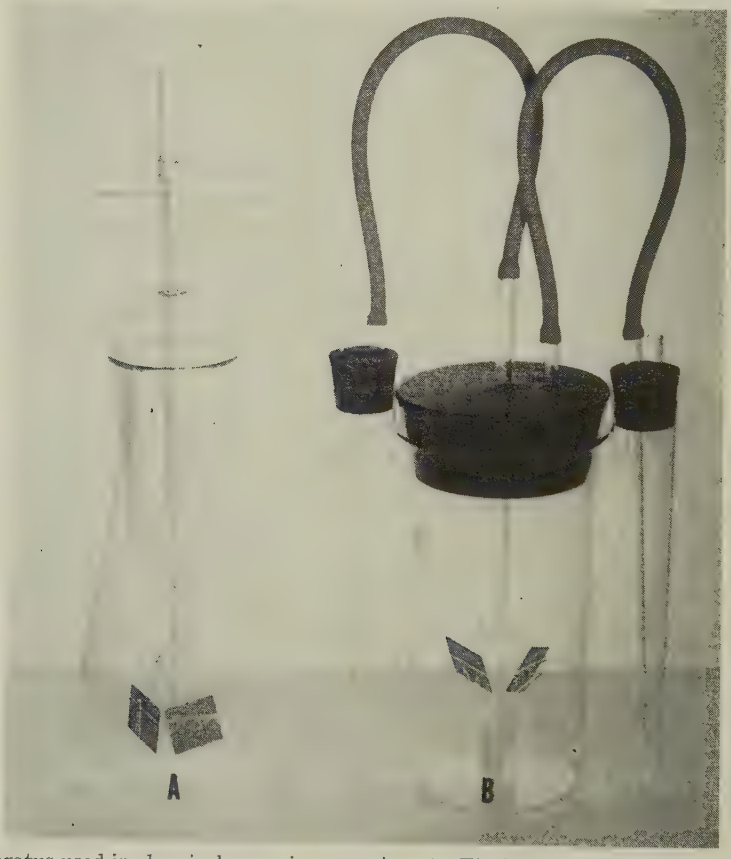

Fig. 1. Apparatus used in chemical corrosion experiments. Flask A was used for ocean water tests and for tests at 60°C and shows aerator–condenser assembly. Flask B was used for tests at 35°C.

ocean water tests and in most tests at 60°C consisted of a 1 l Erlenmeyer flask, a specimen support, and an aerator-condenser assembly (Fig. 1A). Tests at 35°C were conducted in the other apparatus (Fig. 1B). Tests with 9.8 *N* hydrochloric acid at 60°C were also conducted in the modified apparatus. Loss in weight was used as a measure of corrosion. Final acid concentrations were determined in experiments involving acid corrodents. Acid consumption was 6% or less in most concentrations of sulfuric, hydrochloric, and phosphoric acids and in 0.5 *N* nitric acid. However, a 20–35% reduction in concentration occurred at 35°C in 12 *N* hydrochloric and 3 *N*

nitric acid solutions, and at 60°C in 6 *N* and 10 *N* hydrochloric and 2 *N* nitric acid solutions.

Galvanic couple experiments were conducted in the apparatus shown in Fig. 2. The large bottle contained two specimens, each of the two metals involved in the experiment and 550 ml of solution. Specimens were inserted through slits in small rubber stoppers, which fitted tightly in holes in the large stopper. This formed gas-tight seals, yet permitted external connections. Members of each couple were equal in exposed surface area. The upper portion of each specimen was insulated with rubber

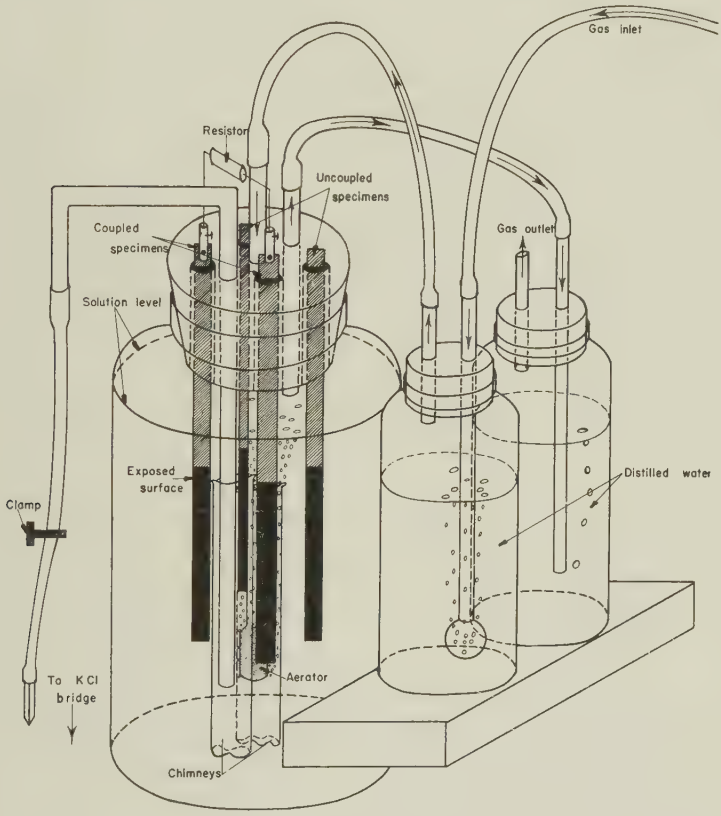

Fig. 2. Apparatus used in galvanic couple corrosion experiments.

tape, leaving 3 in. of length exposed to the solution. Solution level in the specimen bottles was high enough to avoid solution–gas interface effects. Specimens were approximately 0.8 in. apart. One pair of dissimilar specimens was connected through a 1 ohm (±1%) resistor; the other two specimens were not coupled.

Galvanic currents flowing through the couples were determined by measuring voltage drops across the resistor and applying Ohm's law. Voltage drops were measured with a potentiometer and a galvanometer. Galvanic corrosion rates were calculated from average galvanic currents by applying Faraday's law. Galvani ccorrosion rates were averaged for the entire experiment. Weight losses of coupled and uncoupled

metal specimens were determined and used in calculating total corrosion rates. Electrode potentials of each uncoupled specimen and of the couple were measured with an L & N type K-2 potentiometer, a saturated calomel electrode, and a saturated potassium chloride bridge. The apparatus was arranged to measure the potential of the whole specimen, rather than that for a particular point. Electrode potentials are reported on the standard hydrogen electrode scale.

RESULTS

The data now available indicate that vanadium from the three sources has substantially the same corrosion properties. For this reason, the data summarized in this report are not identified as to source of vanadium.

Vanadium is very resistant to corrosion in substitute ocean water, 3% sodium chloride solution, and tap water (College Park, Md.), saturated with air; it is completely resistant to these solutions in the absence of air (Table II). Vanadium corrodes rapidly in 20% ferric chloride solution and at a moderate rate in 5% mercuric chloride solution. It is resistant in 10% sodium hydroxide solution saturated with air and is almost inert in this solution in the absence of air.

At 35°C, vanadium is resistant to corrosion in sulfuric acid solutions (Table III); at 60°C, it is fairly resistant, even in concentrated acid. Vanadium is also resistant to corrosion in hydrochloric acid solutions. Vanadium resists corrosion in 0.5 *N* nitric

TABLE II

VANADIUM IN MISCELLANEOUS REAGENTS, 35°C, 30 DAYS, 4 REPLICATES

Corrodant	*Corrosion rate (m.p.y.)*[d]	
	Air	*He*
Substitute ocean water	0.6[a]	—
3% NaCl	0.4	0.0
Tap water	0.7	0.0
20% $FeCl_3$[b]	3560	3480
5% $HgCl_2$[c]	64	63
10% NaOH[c]	3.9	0.1

[a] Vanadium from commercial supplier 2. Values for vanadium from commercial supplier 1 and Bureau of Mines[1]: air, 0.2; He, 0.0 m.p.y.
[b] Experiments lasted 2.8 days.
[c] Experiments lasted 6 days.
[d] Mils penetration per year, m.p.y.

acid solution at 35°C, but corrodes in 3 *N* acid. At 60°C, corrosion rates are even higher. In general, data for nitric acid solutions are erratic. When corrosion rates for replicates are in substantial disagreement, the values are given separately in the table. Vanadium is resistant to corrosion in phosphoric acid solutions, even in concentrated solutions at 60°C. As a rule, corrosion rates in inorganic acids are not greatly affected by the absence of air. However, at 60°C, corrosion rates are lower in air-free solutions of sulfuric and hydrochloric acids.

Vanadium is very resistant to corrosion in 10% solutions of formic, acetic, lactic, tartaric, and citric acids at 35° and 60°C (Table IV). It is also resistant in 9% oxalic acid. In every instance, corrosion rates are slightly lower in the absence of air.

Corrosion rates published by KINZEL[3,4] pertain to somewhat different concentrations and temperatures but, in general, are quite consistent with the data presented above. However, there is one deviation. KINZEL indicates that, in 20% hydrochloric acid at 70°C, vanadium corrodes more in the absence of air. Data obtained in this investigation indicate that the reverse is true.

TABLE III

VANADIUM IN INORGANIC ACID SOLUTIONS, FLOW OF AIR, 6 DAYS, 4 REPLICATES

Concentration of acid (N)		*Corrosion rate (m.p.y.)*[e]	
		35°C	*60°C*
Sulfuric acid solutions			
0.1	(0.5%)	0.5	—
1.0	(4.8%)	0.6[a]	2.1
3.1	(13.9%)	1.2[a]	—
17.8	(58.8%)	3.9[a]	21.8[b]
—	(97%)[f]	5.8	51.2
Hydrochloric acid solutions			
1.0	(3.6%)	0.6[a]	1.9
2.0	(7.1%)	1.1[a]	—
6.1	(20.2%)	5.2[a]	35.4
9.8	(30.9%)	—	131
11.7	(36.3%)	29.8	—
Nitric acid solutions			
0.5	(3.1%)	1.0[a]	4, 33
2.0	(11.8%)	2.7[a]	>3480[c]
3.0	(17.2%)	<2270[a,d]	—
Phosphoric acid solutions			
—	(10%)	0.4	1.8
—	(50%)	0.9	4.3
—	(85%)	1.0	6.3

[a] Data from earlier publication[1] included for purposes of comparison.
[b] Number of replicates, 8.
[c] Time, 2 to 4 days.
[d] Time, 2 to 4 days; number of replicates, 8; rates for pairs of specimens 98, 20, 2270, 25 m.p.y
[e] Mils penetration per year, m.p.y.
[f] Nominal.

TABLE IV

VANADIUM IN ORGANIC ACID SOLUTIONS, 6 DAYS, 4 REPLICATES

Solution	*Corrosion rate (m.p.y.)*[a]			
	35°C		*60°C*	
	Air	*He*	*Air*	*He*
10% formic	0.5	0.2	1.2	0.8
10% acetic	0.3	0.1	1.7	0.4
10% lactic	0.3	0.1	1.1	0.6
9% oxalic	4.3	1.8	9.8	6.9
10% tartaric	0.4	0.1	1.5	0.5
10% citric	0.2	0.1	0.8	0.3

[a] Mils penetration per year, m.p.y.

Fig. 3 shows results of a typical galvanic couple experiment with vanadium and aluminum 2S-O in 3% sodium chloride with a flow of air. The single (uncoupled) vanadium specimen immediately acquired an electrode potential more noble than that of the single aluminum specimen, and this continued throughout the 15 days.

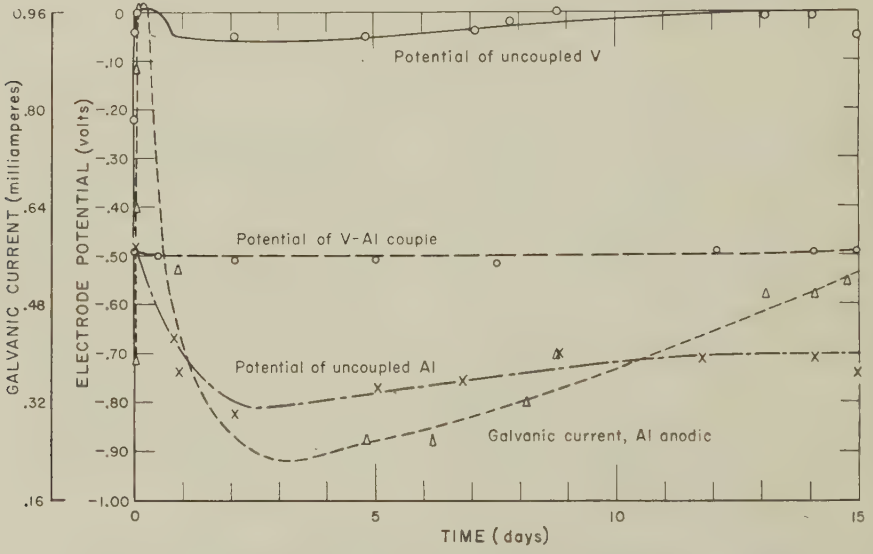

Fig. 3. Vanadium–aluminum (2S-O) couple in 3% sodium chloride solution with flow of air at 35°C (electrode potentials referred to standard hydrogen electrode).

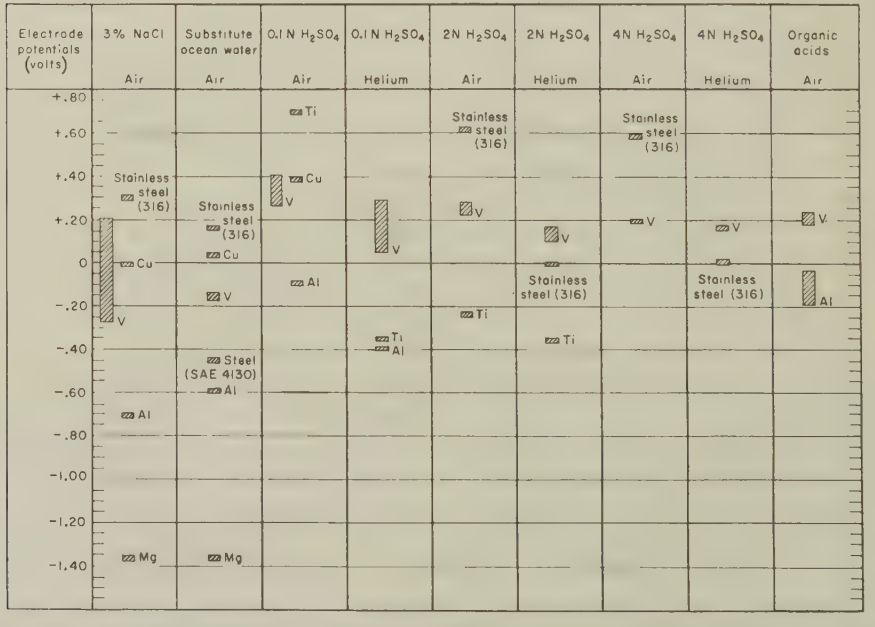

Fig. 4. Single electrode potentials of metals in solutions at 35°C (referred to standard hydrogen electrode). These values are based upon measurements made with the single (uncoupled) specimens during the couple experiments.

TABLE V

CORROSION OF VANADIUM–METAL COUPLES IN CORRODENTS AT 35°C, 15 DAYS

Corrodent	*Second metal*	*Anodic member*	*Galvanic corrosion (m.p.y.) (calc. from current)*	*Corrosion rate, vanadium (m.p.y.) (based on weight loss)*		*Corrosion rate, second metal (m.p.y.) (based on weight loss)*	
				Coupled	*Uncoupled*	*Coupled*	*Uncoupled*
3% sodium chloride solution, flow of air	Magnesium[a]	Magnesium	2952	0.0	1.3	8820	68.8
	Aluminum, 2S-O	Aluminum	14	0.2	0.5	16.4	0.7
	Copper	Vanadium	0[b]	0.8	0.9	3.0	2.9
	Stainless steel, 316	Vanadium	0[b]	0.7	0.7	0.4	0.1
0.1 *N* sulfuric acid, flow of air	Aluminum, 2S-O	Aluminum	34	0.0	2.3	48.5	38.8
	Copper	Copper	28	19.1	30.1	110	73.5
	Titanium	—	0	1.7	1.6	0.0	0.0
0.1 *N* sulfuric acid, flow of helium	Aluminum, 2S-O	Aluminum	26	0.0	0.1	31.0	21.3
	Titanium	—	0	0.0	0.0	0.0	3.3
2.0 *N* sulfuric acid, flow of air	Stainless steel, 316	Vanadium	0[b]	1.5	1.2	0.0	0.0
	Titanium	—	0	0.8	0.5	0.0	60.0
2.0 *N* sulfuric acid, flow of helium	Stainless steel, 316	Stainless steel	6[c]	0.4	0.4	1.4	6.9
	Titanium	Titanium	0[b]	0.2	0.2	0.1	21.8
4.0 *N* sulfuric acid, flow of air	Stainless steel, 316	Vanadium	0[b]	1.0	0.9	0.1	0.1
4.0 *N* sulfuric acid, flow of helium	Stainless steel, 316	Stainless steel	5[d]	0.7	0.5	1.4	16.6
10% formic, flow of air	Aluminum, 2S-O	Aluminum	13	0.0	0.8	16.4	14.2
10% acetic, flow of air	Aluminum, 2S-O	Aluminum	5	0.0	1.1	6.4	4.7
10% citric, flow of air	Aluminum, 2S-O	Aluminum	2	0.0	0.3	2.7	1.1
9% oxalic, flow of air	Aluminum, 2S-O	Aluminum	42	0.2	3.7	70.8	42.7

[a] Experiment lasted 5 days. Coupled magnesium specimen was consumed in one day; corrosion rates for this specimen based on one day.
[b] Galvanic current was too small to measure.
[c] This is the average for the initial 4.06 days. After that, the galvanic current was negligible.
[d] This is the average for the initial 3.75 days. After that, the galvanic current was negligible.

The time–electrode potential curve for the couple fell between the curves for the two single specimens and was somewhat closer to that for the aluminum specimen. Aluminum was the anodic member of the couple. The galvanic current reached a peak in about 5 h, dropped to a low value, then increased at a moderate rate, and eventually reached a steady state.

The steady-state values of the electrode potentials of the single metal specimens in the galvanic corrosion experiments were used in preparing the chart shown in Fig. 4. The chart indicates the relative positions of the electrode potentials of the various metals on the standard hydrogen electrode scale. Direction of flow of measurable galvanic currents generated in any of the couples was consistent with the relative electrode potentials of the single specimens. When the value for the electrode potential of vanadium in a particular solution varied from experiment to experiment, the potential is represented on the diagram by a column. Columns are also used for both vanadium and aluminum in the four organic acids.

Galvanic corrosion experiments at 35°C are summarized in Table V. Vanadium was the anodic (corroding) member of vanadium–stainless steel and vanadium–copper couples in 3% sodium chloride solution with a flow of air. However, the currents were too small to measure, and coupling did not affect any of the three metals. Magnesium was anodic when coupled with vanadium in this environment and corroded very rapidly as a result of contact. The corrosion of vanadium was eliminated as a result of contact with magnesium. Aluminum was the anodic member of the vanadium–aluminum couple and corroded by galvanic action. Vanadium was protected to some extent as a result of contact with aluminum.

Although titanium is more noble than vanadium in 0.1 *N* sulfuric acid solution with a flow of air (Fig. 4), the vanadium–titanium couple did not generate a current and neither metal was affected by the contact. Copper was the anodic member of the vanadium–copper couple in this environment and corroded at a substantial rate as a result of contact with vanadium. The single vanadium specimen corroded in this experiment, probably as a result of the presence of copper ions; the coupled vanadium specimens corroded at a lower rate. Aluminum corroded at a substantial rate as a result of contact with vanadium in this solution and the corrosion of vanadium was eliminated as a result of the contact.

Aluminum was also the anodic member of the vanadium–aluminum couple immersed in air-free 0.1 *N* sulfuric acid solution and corroded at a substantial rate by galvanic action. There was no detectable galvanic current in the vanadium–titanium couple immersed in this environment, although vanadium is much more noble than titanium (Fig. 4). However, the normal corrosion of titanium was eliminated as a result of the contact. This results from the tendency for titanium to become anodically polarized.

Stainless steel, type 316, was the anodic member of the vanadium–stainless steel couple in 2 *N* sulfuric acid solution with a flow of air, but there was no detectable galvanic current, and neither vanadium nor stainless steel was affected by contact. The vanadium–titanium couple did not generate a current in this environment, although titanium was less noble than vanadium. The corrosion of vanadium was not affected by the contact. However, the corrosion of titanium, normally rapid in this solution, was eliminated as a result of contact with vanadium. This is the result of anodic polarization.

Stainless steel was the anodic member of the vanadium–stainless steel couple in 2 *N* sulfuric acid with a flow of helium and corroded anodically for about one-third of the experimental period. The corrosion rate of vanadium was not changed by the contact, and in spite of the galvanic corrosion of the stainless steel, its total corrosion was less than normal. Evidently, this is another instance of anodic polarization. The normal corrosion of stainless steel was apparently eliminated as a result of contact with vanadium. There was no measurable current in the vanadium–titanium couple in this environment, although titanium was anodic. The corrosion of vanadium was not affected by the contact with titanium, but the normal corrosion of titanium was almost eliminated because of the contact and the resulting anodic polarization.

In 4 *N* sulfuric acid with a flow of air, vanadium was the anodic member of the vanadium–stainless steel couple, but the galvanic current was too small to measure, and neither metal was affected by the contact. In the absence of air, stainless steel was the anodic member, and there was a flow of current during the first 3.75 days of the experiment. The normal corrosion of stainless steel was greatly decreased by the contact because of anodic polarization. The corrosion of vanadium was not affected by the contact.

In formic, citric, acetic, and oxalic acids, aluminum was the anodic member of the vanadium–aluminum couples and corroded by galvanic action. Its normal corrosion was decreased as a result of the flow of current. Corrosion of vanadium was generally eliminated as a result of the contact.

CONCLUSIONS

1. Vanadium is resistant to corrosion in substitute ocean water, 3% sodium chloride solution, tap water, and 10% sodium hydroxide solution. It corrodes rapidly in 20% ferric chloride solution and at a moderate rate in 5% mercuric chloride solution.

2. Vanadium is relatively resistant to corrosion in phosphoric, sulfuric, and hydrochloric acids, but corrodes rapidly in nitric acid.

3. Vanadium is almost inert in 10% formic, acetic, lactic, tartaric, and citric acids. It is resistant to corrosion in 9% oxalic acid.

4. In the absence of air, vanadium corrodes less in substitute ocean water, 3% sodium chloride, tap water, 10% sodium hydroxide, and organic acids. Air has little, if any, effect on the corrosion behavior of vanadium in inorganic acids at 35°C. However, at 60°C, in the more concentrated sulfuric and hydrochloric acid solutions, the absence of air results in substantial decreases in the corrosion rate of vanadium.

5. Vanadium is protected by contact with magnesium, aluminum, or SAE 4130 steel. Vanadium protects copper in substitute ocean water but has no effect in 3% sodium chloride solution. Vanadium and stainless steel are usually not affected by contact. However, the corrosion of stainless steel is decreased by contact with vanadium in air-free sulfuric acid solutions because of its tendency toward anodic polarization. The corrosion of titanium in contact with vanadium in sulfuric acid solutions is almost eliminated.

REFERENCES

1 David Schlain, Charles B. Kenahan and Walter L. Acherman, *Corrosion*, 14 (1960) 114.
2 *ASTM Standards*, Part 7, American Society for Testing Materials, Philadelphia, Pa., 1952, pp. 1241–1242.
3 A. B. Kinzel, *Metal Progr.*, 58 (1950) 315.
4 W. Rostoker, *Metallurgy of Vanadium*, J. Wiley & Sons, Inc., New York, 1958, p. 134.

THE CONSTITUTION OF SOME VANADIUM-BASE BINARY AND TERNARY SYSTEMS AND THE AGEING CHARACTERISTICS OF SELECTED TERNARY ALLOYS*

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SUMMARY

To promote development of vanadium-base alloys, binary (V–Sn, V–Hf, V–W, V–Re, V–Th) and ternary systems (V–Ti–Nb, V–Ti–Mo, V–Ti–Ta, V–Ti–W, V–Ti–Be, V–Ti–O, V–Ti–Si) were investigated to determine the extent of the vanadium-rich solid solution between 800° and 1500°C, the character of the second phase in equilibrium with the solid solution, and melt reactions. The age hardening of selected V–Ti–Be, V–Ti–O, and V–Ti–Si alloys was studied at 550°, 650° and 750°C.

INTRODUCTION

The purpose of this research work was to develop a background of information for further vanadium alloy development. The information of most use in alloy development concerns the extent of possible solid solution additions, the phases appearing when the solid solubility is exceeded, potential precipitation-hardening systems, and the solidification reactions.

The rudimentary phase relationships of binary systems V–Sn, V–Hf, V–W, V–Re, and V–Th and ternary systems V–Ti–Nb, V–Ti–Mo, V–Ti–Ta, V–Ti–W, V–Ti–Be, V–Ti–O, and V–Ti–Si are reported in this paper. It is emphasized that there is no intent to define the complete phase relationship in any one system. The objectives of the program were to be met by the determination of the following information:

(1) extent of the solid solution field at temperatures of 800°, 1000°, 1200°, and 1500 °C;

(2) character of the second phase in equilibrium with the solid solution;

(3) melt reaction, where possible;

(4) precipitation kinetics in selected compositions from systems V–Ti–Be, V–Ti–O, and V–Ti–Si.

In general, the investigation was restricted to vanadium-rich alloys, but in several cases work on compositions with less than 50 wt. % V was necessary to resolve certain problems.

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EXPERIMENTAL MATERIALS AND METHODS

The highest purity metals were used in this work. The greatest problem concerned the quality of vanadium metal. The calcium-reduced vanadium metal contained 0.15–0.20 wt. % oxygen, but was the best that could be obtained in the quantities required for the program. In view of the previous success of the electron-gun refining process on niobium, it was planned to refine by this means. The theory of electron-gun refining was not well known at the time; now, it is apparent that metals of high volatility cannot be refined appreciably (unless the oxide is even more volatile). Table I shows that this refining was unsuccessful. For critical alloy compositions higher purity vanadium was used: iodide vanadium and electrolytic vanadium. Additional pure vanadium was obtained by refining with rare-earth metals. Table I summarizes the supplier and purity of the vanadium metal.

TABLE I

ANALYSIS AND SUPPLIER OF VANADIUM METAL

Type of metal	*Analysis (p.p.m.)*				*Supplier*
	Oxygen	*Nitrogen*	*Hydrogen*	*Others*	
Calcium-reduced	1265	383	28	n.d.	Vanadium Corp. of America
Electron-gun refined*	1500	84	5	n.d.	Stauffer-Temescal Corporation
Refined with La*	166	128	15	n.d.	Armour Research Foundation
Refined with Gd*	170	174	22	n.d.	Armour Research Foundation
Electrolytic	550	n.d.**	n.d.	>1150	Bureau of Mines
Iodide	100	<50	n.d.	> 900	Iowa State College

* From calcium-reduced vanadium of the Vanadium Corporation of America.
** Not determined.

TABLE II

SUPPLIER AND PURITY OF ALLOYING ELEMENTS

Metal	*Supplier*	*Grade or purity*
Tin	Vulcan Detinning Company	Electrolytic, 99.998% pure
Hafnium	U.S. Atomic Energy Commission	Iodide grade, <1% Zr
Thorium	Metal Hydrides	Iodide grade
Tungsten	Fansteel Metallurgical Corp.	Powder, electron-gun refined
Rhenium	Jarrel-Ash Company	Spectrographic, 99.9+% pure
Titanium	Foote Mineral	Iodide grade
Niobium	DuPont	Electron-gun refined
Molybdenum	Fansteel Metallurgical Corp.	Powder, electron-gun refined
Tantalum	Fansteel Metallurgical Corp.	Powder, electron-gun refined
Silicon	DuPont	Solar grade, 2–3 p.p.m. impurities
Beryllium	Beryllium Corp.	Flake, 99.6% Be

The other metals are listed in Table II with the identification of the source and grade.

The standard alloy preparation consisted of melting a 10-g charge four to six times in a nonconsumable-electrode, water-cooled copper crucible, arc-melting furnace described elsewhere[1]. The ingot or button was inverted between each fusion. The efficiency of the melting operation was judged by the extent of any weight changes

during the melting, which rarely exceeded 0.010 g. A second check of the melting was made by quarter-sectioning the button and examining for homogeneity. Whenever possible, the alloys were deformed prior to isothermal annealing. Solution anneals at 1500°C prior to the isothermal anneals were required in some cases where the melt reaction was such that segregation resulted.

The specimens were placed in annealing bulbs, evacuated, flushed with argon, evacuated, and sealed. Vycor was used for the 800° and 1000°C anneals, and quartz was used at 1200°C. The 1500°C treatments were made in a vacuum annealing furnace previously described[2]. The following annealing times were applied at the indicated temperatures:

temperature (°C)	*time (h)*
800	360
1000	48
1200	16
1500	2.5

These follow an Arrhenius plot relationship, so that if the times are adequate at low temperatures, they are likely to be adequate at other temperatures. Many specimens were given repeat anneals to double the above times to determine the adequacy of these anneals.

In the case of melts involving the refractory metals (molybdenum, tantalum, and particularly rhenium and tungsten) difficulty was experienced with incomplete solution of the refractory metal. One reason for this is believed to be the high vapor pressure of vanadium, which is so high that the metal boils freely under the conditions in the arc furnace, thereby preventing any further increase of temperature. One solution to this problem was found to be through master alloys; the refractory metal was placed on top of the vanadium so that it was directly under the arc. In this way the melt at the temperature of the higher melting point component flowed down over the vanadium, resulting in extremely rapid solution. After melting and remelting, the crushed ingot appeared free of undissolved constituents.

The routine examinations performed on the alloys were (a) metallographic examination as cast and annealed; (b) X-ray diffraction of powder specimens; and (c) incipient melting point determinations. The metallography and X-ray diffraction followed normal practice and need no elaboration. The incipient melting point determinations were performed in a vacuum annealing furnace described in detail elsewhere[2].

Specimen preparation for the precipitation kinetics studies and the experimental methods are discussed in the corresponding part of this paper.

The system vanadium–tin

An intermediate phase V_3Sn occurs at 43.71 wt. % Sn. This phase has been found to have a *beta*-tungsten cubic structure having a lattice parameter $a = 4.94 \pm 0.01$ Å. Tin enters into solid solution at least up to 20 wt. % Sn[3,4]. It has been suggested that V_3Sn occurs at 38.5 wt. % (21.2 at. %) Sn rather than at its stoichiometric composition (25 at. %) and that it forms peritectically at 1300°C (Fig. 1).

Vanadium–tin alloys were prepared with tin contents increasing in 5% steps up to 45 wt. %.

The solubility limit was found to be between 19 and 20 wt. % Sn for alloys made with calcium-reduced vanadium and varied imperceptibly between 800° and 1500°C. Alloys made with iodide grade vanadium yielded similar results.

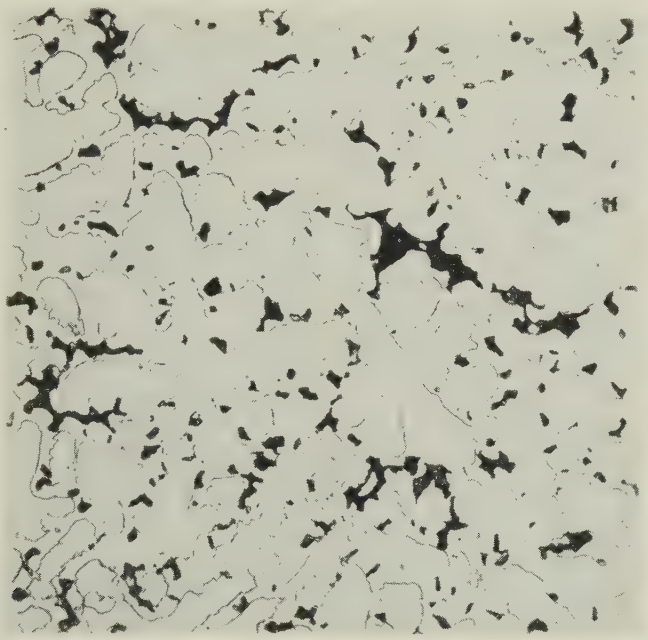

Fig. 1. V–35 wt. % Sn alloy. As-cast structure. Incompleted peritectic reaction. (× 500)

The two-phase field containing the primary vanadium phase extended from 20 to 40–45 wt. % Sn. An X-ray analysis verified that the phase in equilibrium with primary vanadium had a *beta*-tungsten type of structure.

Metallographic examination indicated that the intermediate phase was formed by a peritectic reaction (Fig. 1).

The system vanadium–hafnium

The existence of the f.c.c. intermetallic compound at 63.7 wt. % Hf has been established. This phase is cubic and isotypic with $MgCu_2$[5].

The solubility of hafnium in vanadium was established metallographically on specimens annealed at 1500°, 1200°, 1000°, and 800°C. Alloy V–7.0 wt. % Hf was found to be single phase at 1500°C. Some dispersed precipitate along the subgrain boundaries of this specimen suggested reduced solubility with decreasing temperature. Alloy V–8.0 wt. % hafnium annealed at 1500°C contained an interdendritic second phase. Thus, the solubility of hafnium in vanadium at 1500°C is between 7.0 and 8.0 wt. %.

The solubility of hafnium decreased with decreasing annealing temperatures. At

1200°C it is between 4.0 and 5.0 wt. % Hf, and at 1000°C it is less than 2.0 wt. % Hf.

Metallographic examination of alloys in the range 10.0–50.0 wt. % Hf on specimens in cast condition was carried out to reveal the melt reaction of the system. The structure exhibited primary dendrites and interdendritic eutectic (Fig. 2). This sug-

Fig. 2. V–25 wt. % Hf alloy. As-cast structure. Primary dendrites and interdendritic eutectic. (× 500)

gested an eutectic-type equilibrium on the vanadium-rich side of the HfV_2 intermetallic. Incipient melting point determinations were carried out on alloys in the composition range 10.0–50.0 wt. % Hf to obtain the eutectic temperature. The incipient melting points determined showed a considerable scatter, but in all cases they were lower than the melting point of the vanadium. The eutectic temperature was set tentatively at 1600°C. Alloy V–53.0 wt. % Hf was used to determine the melting point of the intermetallic compound. The specimen did not melt up to 2000°C; therefore, the melting point of HfV_2 has to be higher than 2000°C.

Alloys in the composition range of 57.0–90.0 wt. % Hf exhibited a two-phase structure with primary dendrites and interdendritic eutectic. Incipient melting point determinations gave the eutectic temperature 1550° ± 15°C. From the relative amount of the eutectic found in the metallographic specimens the composition of the eutectic was set tentatively between 80.0 and 90.0 wt. % Hf.

X-ray diffraction was carried out on alloys V–20.0 Hf, V–40.0 Hf, and V–57.0 Hf. The alloys V–20.0 Hf and V–40.0 Hf exhibited identical structure: the diffraction lines of vanadium and HfV_2 were found. In alloy V–57.0 Hf the diffraction lines of the HfV_2 intermetallic and the hafnium metal were identified.

A tentative vanadium–hafnium phase diagram is proposed in Fig. 3. According to the existing experimental evidence, a eutectic is shown between the vanadium and HfV_2 intermetallic compound and between the HfV_2 and hafnium metal.

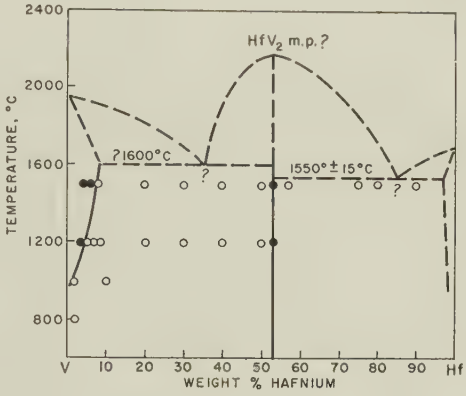

Fig. 3. Tentative vanadium–hafnium phase diagram. ● Single-phase; ○ two-phase.

The system vanadium–rhenium

A two-phase region extending between 38 and 60 at. % Re was reported to exist on the basis of annealing a series of alloy compositions at 1200°C[6]. No intermediate phases were reported.

An initial series of compositions prepared using the pure metals for alloys was found to be heterogeneous. These alloys were, therefore, combined into one larger sized ingot which was melted repeatedly until it was found to be homogeneous. This ingot, containing 81.9 wt. % Re, was used as a master alloy.

Alloys containing 20, 40, 60, 81.9, 90, 92, 94, 96 and 98 wt. % Re were prepared using the above master alloy with the required amounts of one or the other of the pure metals to obtain the desired compositions.

Examination of the alloys after melting revealed, in some cases, incomplete solution of the more refractory charge materials in spite of the use of the master alloy. Alloys were remelted as required.

Metallographic examination of the alloys after homogenizing and annealing heat treatments indicated the solubility of rhenium in vanadium to be between 85 and 90 wt. % Re. The variability in solubility between 800° and 1500°C was evidently within this range of composition. The solubility of vanadium in rhenium was found to be less than 2 wt. %.

The alloys containing between 90 and 98 wt. % Re gave evidence of peritectic melt reactions. An intermediate phase of a composition of approximately 92 wt. % Re is formed from the melt and is stable to a temperature somewhere between 1200° and 1500°C (Fig. 4). Below this temperature it undergoes a eutectoid decomposition forming b.c.c. vanadium and h.c.p. rhenium. The diffraction pattern of the high-temperature phase indicates it to be a complex tetragonal structure with a c/a ratio of 1.515 and an a value of 9.42 Å. This phase thus appears to be very similar to the σ group of phases.

Because of the high temperatures that probably would be involved no effort was made to determine the temperature of the peritectic melt reactions. A check of the 20 and 40 wt. % Re compositions indicated their melting points to be above that of pure vanadium; therefore, no melting point exists in this system lower than the melting point of pure vanadium.

The tentative vanadium–rhenium phase diagram is presented in Fig. 5.

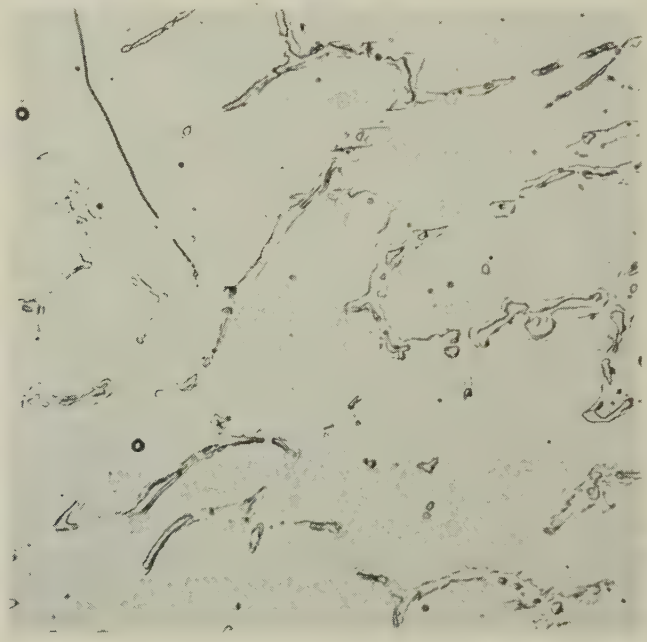

Fig. 4. V–92 wt. % Re alloy. Annealed at 1500°C for 2 h. Peritectically formed σ-phase and solid solution. (× 500)

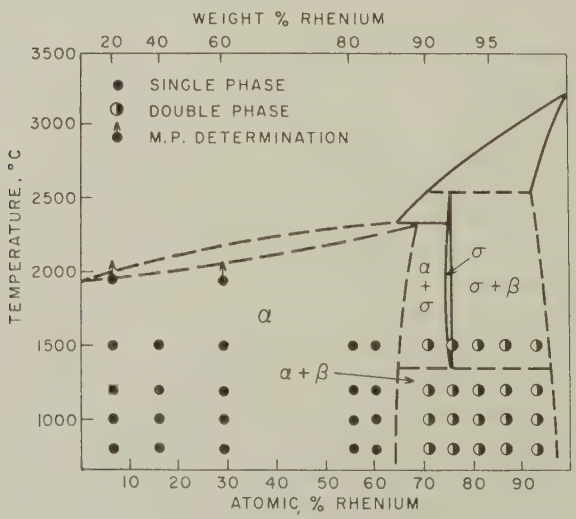

Fig. 5. Tentative vanadium–rhenium phase diagram.

The system vanadium–thorium

A simple eutectic system has been reported. The eutectic composition is about 95 wt. % Th[7] and the eutectic temperature is 1400° ± 15°C. The unfavorable size factor would predict little solubility, and this has been so reported[8].

A series of alloys with increasing thorium contents was prepared and examined. The results verified the findings above.

Thorium, an actinide element, deoxidizes vanadium. All the low-thorium alloys contained about the same amount of ThO_2 and possessed clean vanadium matrices.

The solubility limit, as determined with the use of calcium-reduced vanadium, was between 2 and 3 wt. % Th. A consideration of the fact that over 1 wt. % Th can be effectively removed from the metallic phases by the oxygen present in the calcium-reduced vanadium indicates the above solubility limit to be too high. Accordingly, alloys containing 1, 1.5, 2, and 2.5 wt. % Th were prepared from iodide grade materials. Examination of these alloys indicated the solubility of thorium in vanadium to be less than 1 wt. % up to the eutectic temperature.

The solubility of vanadium in thorium is less than 2.5 wt. % up to the eutectic temperature.

Thorium is reported to undergo transformation from b.c.c. to a f.c.c. structure at 1425°C[8]. Experimental observations did not indicate that this was of any significance to the vanadium side of the diagram.

The system vanadium–niobium–titanium

Niobium and vanadium depress the temperature of stability of the h.c.p. phase of

Fig. 6. V–35 wt. % Nb–12 wt. % Ti alloy. Annealed at 800°C for 360 h. Single-phase structure. (× 100)

titanium, and both form a continuous series of solid solutions with *beta*-titanium[3,9–13].

The presence of small amounts of a grain-boundary precipitate in vanadium alloys containing 30–40 wt. % Nb after annealing 170 h at 900°C was reported, and the possibility of the presence of a *sigma*-type phase was considered[3,5].

Metallographic examination of the alloys V–20 wt. % Nb, V–20 wt. % Nb–12 wt. % Ti, V–20 wt. % Nb–25 wt. % Ti, V–35 wt. % Nb, V–35 wt. % Nb–7 wt. % Ti, V–35 wt. % Nb–12 wt. % Ti, and V–48 wt. % Nb after annealing at the required temperatures failed to reveal any trace of a second phase (Fig. 6).

From the above it is concluded that the vanadium–niobium–titanium system forms a continuous series of solid solutions above 800°C, except in the titanium-rich corner where *alpha*-titanium is stable up to 885°C.

The systems vanadium–molybdenum and vanadium–molybdenum–titanium

Vanadium and molybdenum are miscible with *beta*-titanium[3,9–14].

Molybdenum and vanadium form a continuous series of solid solutions at elevated temperatures[15]. An unidentified intermediate phase has been reported[3], but this has been questioned[16].

A master alloy containing 49.5 wt. % Mo was made using high-purity vanadium.

The following series of alloy compositions (all concentrations in wt. %), chosen so as to cover the probable extent of the stability of the reported intermediate phase, was prepared for study:

V–5 Mo	V–10 Mo–10 Ti	V–40 Mo–20 Ti
V–10 Mo	V–20 Mo–10 Ti	V–50 Mo–10 Ti
V–20 Mo	V–20 Mo–20 Ti	V–60 Mo–10 Ti
V–40 Mo	V–20 Mo–30 Ti	
V–49.5 Mo	V–30 Mo–20 Ti	
V–60 Mo	V–40 Mo–10 Ti	

Metallographic examination of these alloys after homogenizing and annealing at the required temperatures failed to reveal any trace of a second phase.

The reported second phase was said to have been observed as a grain-boundary precipitate after annealing at 900°C for 170 h[3]. An Arrhenius plot of the heat treatment temperatures used compared with the 900°C–170 h anneal indicates that, to be equivalent, the 800°C annealing time should have been 750 h.

To check more closely as to whether a second phase is precipitated on prolonged annealing, an 800°C anneal would have required excessive time; a 1000°C anneal might well have been above the upper temperature limit of stability of this second phase. It was decided simply to repeat the 900°C–170 h anneal. A V–40 wt. % Mo alloy was used.

No second phase was observed and, accordingly, it was concluded that the vanadium–molybdenum and vanadium–molybdenum–titanium systems form a continuous series of solid solutions (Fig. 7).

The system vanadium–tantalum–titanium

Beta-titanium and vanadium form a continuous series of solid solutions[3,9,10].

Beta-titanium and tantalum are completely miscible[12,17,18].

At elevated temperatures tantalum and vanadium form a continuous series of solid

Fig. 7. V–40 wt. % Mo alloy. Annealed at 900°C for 340 h. Single phase. (× 100)

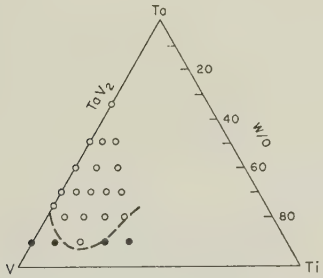

Fig. 8. V–Ti–Ta system. Isothermal section at 800°C. ● Single-phase; ○ two-phase.

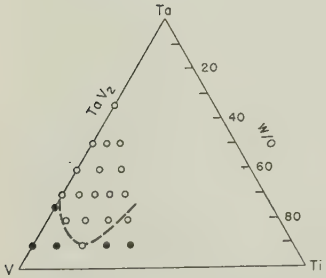

Fig. 9. V–Ti–Ta system. Isothermal section at 1000°C.

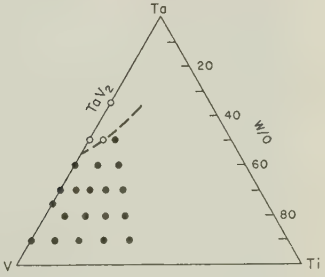

Fig. 10. V–Ti–Ta system. Isothermal section at 1200°C.

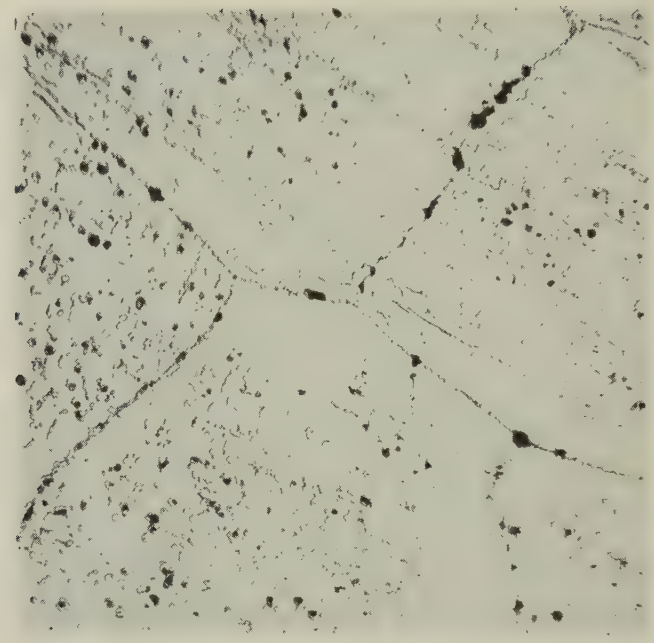

Fig. 11. V–30 wt. % Ta alloy. Annealed at 800°C for 720 h. Second phase is the TaV_2 precipitate. (× 500)

Fig. 12. V–16 wt. % Ti–10.0 wt. % Ta. Annealed at 800°C for 720 h. Two-phase structure, second phase is the TaV_2 compound. (× 500)

solutions[3]. The intermediate phase TaV_2, 64 wt. % Ta, decomposes at 1320°C to form the solid solution[19]. TaV_2 is cubic and isotypic with $MgCu_2$ and has a lattice parameter of $a = 7.162$ Å[20].

The above indicated that in the vanadium–tantalum–titanium system solid-solution alloys are probably formed except in the composition range in tantalum- and vanadium-rich alloys where TaV_2 is stable.

Examination of the alloys after proper heat treatments indicated the limit of stability of TaV_2 to be as shown in Fig. 8, 9 and 10.

The peculiar shape of the solubility boundary at 800° and 1000°C (Figs. 8 and 9) merits discussion. It was considered unlikely, at first, that the diagram was as the initial alloys indicated. Additional alloys made with rare-earth metal deoxidized vanadium, however, led to similar conclusions. Photographs of the V–30 Ta and the V–16.8 Ti–10 Ta alloys annealed at 800°C for 120 h are included to show the similarity of the precipitate (Figs. 11 and 12). The dark-appearing phases are rare-earth metal inclusions. As can be seen in Fig. 12, the small amount of precipitate did not allow for the verification of the presence of TaV_2 by X-ray analysis.

The binary alloys of compositions up to 40 wt. % Ta did not reveal precipitation after 360 h at 800°C, whereas the 30 wt. % Ta alloy was found to contain TaV_2 after annealing at 1000°C. The precipitation of TaV_2, therefore, appears to be a very sluggish reaction in dilute vanadium–tantalum alloys. Accordingly, compositions in which the precipitation of TaV_2 was considered possible were cold pressed 25% and re-annealed. Many of these alloys were then found to contain TaV_2.

The systems vanadium–tungsten and vanadium–tungsten–titanium

A two-phase field was reported to exist at about 50 wt. % W in the vanadium–tungsten system[3].

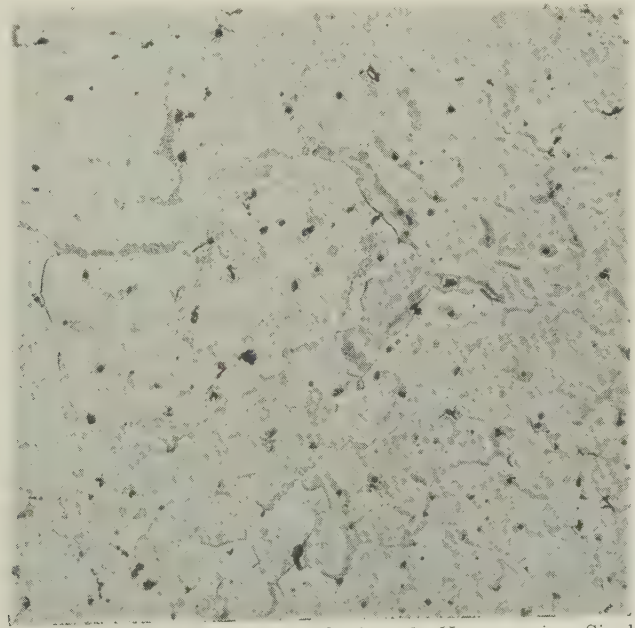

Fig. 13. V–60 wt. % W alloy. Annealed at 1500°C for 2 h. Heavy coring. Single-phase. (× 150)

Beta-titanium dissolves about 50 wt. % W at 1880°C[17,21]. The solubility limit decreases to about 28 wt. % at 715°C. No intermediate phases were found.

Compositions chosen for investigation in these systems were based on the expected extent of the reported two-phase field in the vanadium–tungsten system and the way this boundary would extend through the ternary to join, in some way, the boundaries of the W + β-Ti field in the tungsten–titanium system. All alloys were found to be single phase. Very severe coring, not overcome by homogenizing heat treatments, was exhibited by the alloys (Fig. 13). The heavy coring can be explained by the large difference of the melting points of the components.

It is concluded that vanadium and tungsten form a continuous series of solid solutions. The contention is supported by the recent work of KIEFFER *et al.*[22].

A miscibility gap, of necessity, exists on the titanium–tungsten side of the ternary diagram. Compositions investigated indicate that it does not extend beyond 15 wt. % V into the ternary system.

Figure 14 shows, schematically, the appearance of the isothermal section at 800°C and above.

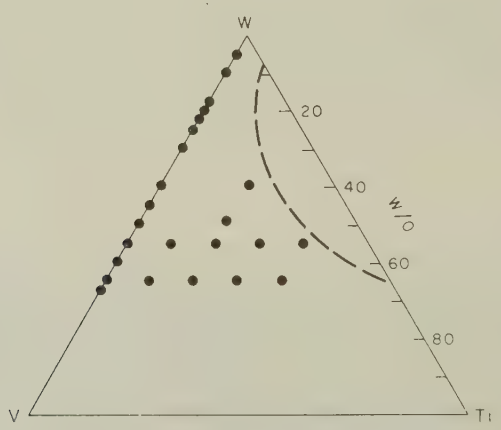

Fig. 14. V–Ti–W system. Schematic isothermal section at 800°C and above. ● Single-phase.

The system vanadium–titanium–beryllium

The vanadium-rich side of the vanadium–beryllium binary system was reported to be an eutectic type[3,23]. The eutectic exists between V and VBe_2 at about 15 wt. % Be and at about 1650°C.

The solubility of beryllium in vanadium–titanium solid solution up to 50 wt. % Ti was determined metallographically in the temperature range 800°–1500°C. Figures 15 and 16 present the boundary of the ternary solid solution at 1500°C and 1000°C temperature.

Metallographic examination of the alloy compositions indicated that the phase in equilibrium with the solid solution within the composition range investigated is the VBe_2 intermetallic. This was confirmed by X-ray diffraction analysis. A tentative phase field boundary starting out of the composition of the VBe_2 intermetallic compound is shown in insert of Fig. 16.

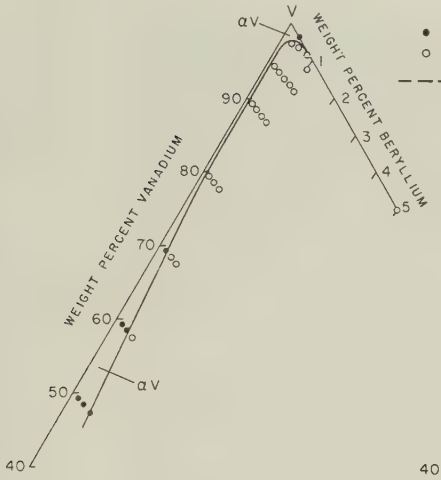

Fig. 15. V–Ti–Be system. Isothermal section at 1500°C.

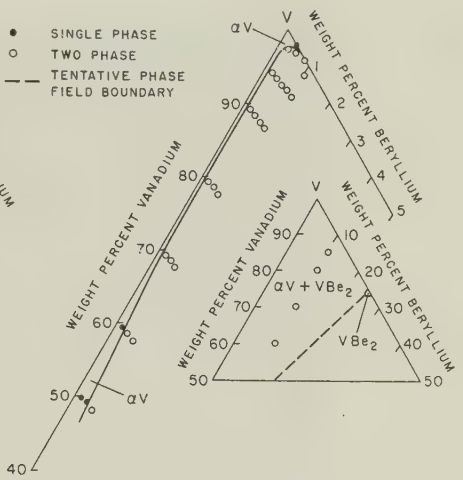

Fig. 16. V–Ti–Be system. Isothermal section at 1000°C.

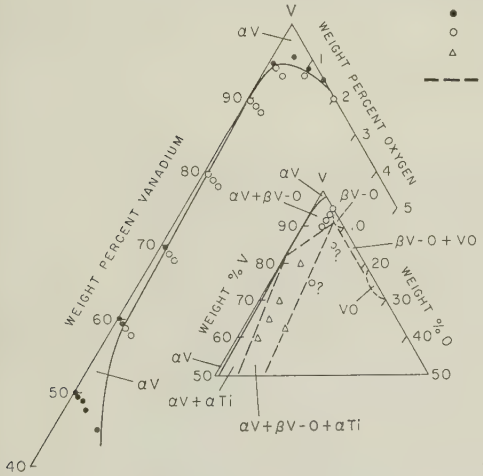

Fig. 17. V–Ti–O system. Isothermal section at 1200°C.

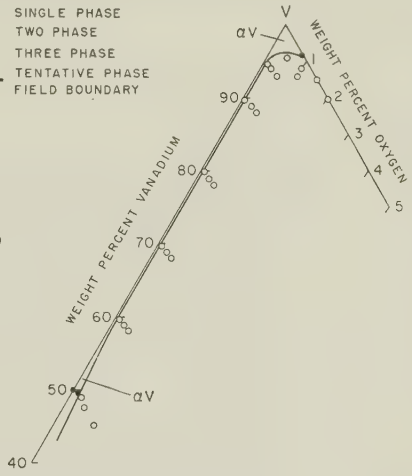

Fig. 18. V–Ti–O system. Isothermal section at 800°C.

The system vanadium–titanium–oxygen

Two conflicting phase diagrams have been proposed on the vanadium–oxygen system[3,24,25]. The titanium–oxygen system has been described in detail[25].

The boundary of the single phase α-vanadium solid solution was determined metallographically at 1500°, 1200°, 1000° and 800°C temperatures. Figures 17 and 18 show the boundary of the single-phase α-vanadium at 1200°C and 800°C temperatures, indicating decreasing oxygen solubility with decreasing temperature.

Fig. 19. V–50.0 wt. % Ti–0.07 wt. % O. Annealed at 1200°C and quenched. Single phase. (× 500)

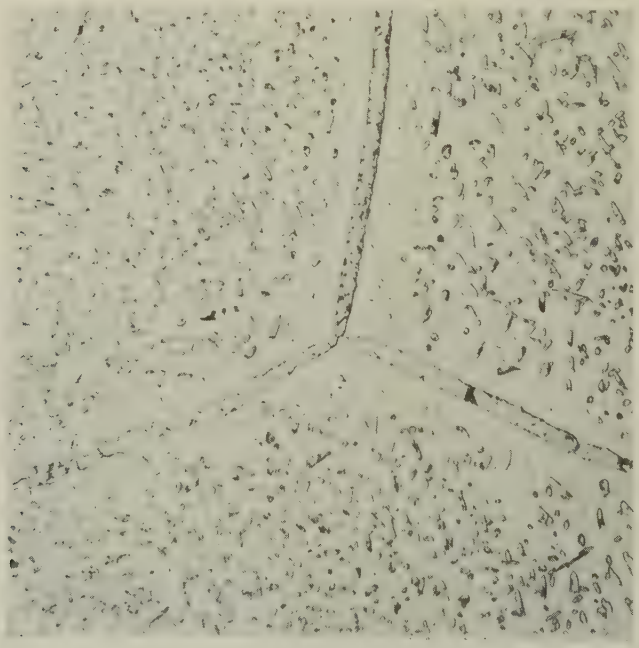

Fig. 20. V–50.0 wt. % Ti–0.07 wt. % O. Annealed at 800°C for 360 h and quenched. Note coagulation of second phase at grain boundaries. (× 500)

The existence of the phases in equilibrium with the α-vanadium solid solution was determined by X-ray diffraction, and the tentative phase field boundaries are shown in the insert of Fig. 17. The α-titanium has remarkably great stability, which can be explained by the strong stabilizing effects of the oxygen on the α-titanium[25]. Figures 19 and 20 illustrate the precipitation of α-titanium at 800°C in alloy V–50.0 wt. % Ti–0.07 wt. % O, which is single-phase solid solution at 1200°C.

The system vanadium–titanium–silicon

According to earlier suggestions[3,26 30], the existence of three intermediate phases was confirmed in the vanadium–silicon binary system: V_3Si has the "β-W" (A 15) type of structure; the compound V_5Si_3 has a tetragonal Ni_3P type of structure (c/a = 0.505); and VSi_2 was found to have the hexagonal $CrSi_2$ (C40) type of structure (c/a = 1.359)[25].

Fig. 21. V–Ti–Si system. Isothermal section at 1500°C.

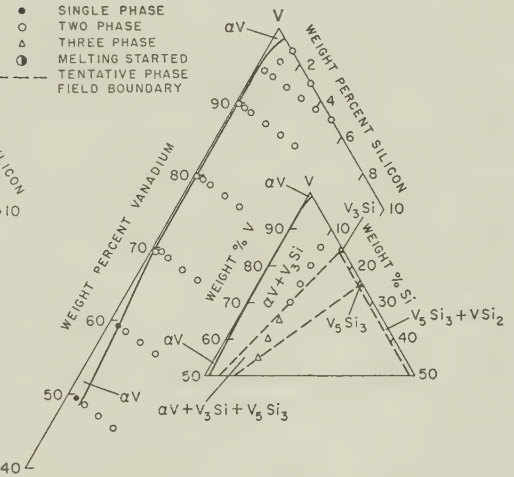

Fig. 22. V–Ti–Si system. Isothermal section at 1000°C.

The eutectic composition between vanadium and V_3Si occurs at 7.5 wt. % Si, and V_3Si phase appears to form by peritectic reaction[3,30].

Phases existing in the titanium–silicon system[25] were not found in the investigated partial vanadium–titanium–silicon ternary system.

The solid solubility of silicon in the completely miscible vanadium-titanium solid solution was established by microscopic examination of different alloy compositions after annealing at 1500°, 1200°, 1000°, and 800°C. Figures 21 and 22 present the boundary of the single-phase field at 1500°C and 1000°C.

Few alloys started to melt during annealing at 1500°C. Incipient melting point determinations were carried out on the specimens, and the results are listed in Table III.

TABLE III

Alloy compositon (wt.%)	*Incipient melting point (°C)*
V–25.0 Ti–10.0 Si	1475 ± 15
V–30.0 Ti–10.0 Si	1365 ± 15
V–35.0 Ti–10.0 Si	1365 ± 15
V–47.0 Ti– 3.0 Si	1500 ± 15

The microscopic examination was quite informative regarding the phases in equilibrium with the ternary solid solution. X-ray diffraction on powdered alloys annealed at 1000°C and water quenched was used to confirm the findings of the metallographic examinations.

The phase-field boundaries are tentatively drawn (dotted lines) into the insert of Fig. 22, although no further effort was made toward a quantitative delineation of the multiphase fields.

PRECIPATION KINETIC STUDIES IN SELECTED ALLOY COMPOSITIONS OF THE SYSTEMS V–Ti–O, V–Ti–Be AND V–Ti–Si

Experimental methods

On the basis of the phase-equilibrium investigations nine alloy compositions of systems V–Ti–O, V–Ti–Be, and V–Ti–Si were selected for a study of the precipitation-hardening behavior of promising vanadium-base alloys.

Table IV summarizes the compositions of the selected alloys and the identity of the precipitating phase.

TABLE IV

SUMMARY OF THE AGE HARDENING OF THE SELECTED V–Ti–O, V–Ti–Be AND V–Ti–Si ALLOYS

Alloy composition (wt. %)	*Precipitating phase*	*Hardness after soln. anneal (VPN)*	*Aged at 550°C*		*Aged at 650°C*		*Aged at 750°C*	
			Maximum hardness (VPN)	*Time to obtain max. hardness (h)*	*Maximum hardness (VPN)*	*Time to obtain max. hardness (h)*	*Maximum hardness (VPN)*	*Time to obtain max. hardness (h)*
V–4.8 Ti–0.2 O	β-V	240	325	40	338	1	335	6
V–1.5 Ti–0.5 O	β-V	397	432	7	435	1/10	430	12
V–10.0 Ti–0.14 O	β-V	295	358	4	344	1	344	2
V–4.6 Ti–0.4 Be	VBe_2	200	none	>200	288	1	285	6
V–1.0 Ti–0.5 Be	VBe_2	175	none	>200	300	1	285	12
V–10.0 Ti–0.4 Be	VBe_2	900–1000	—	—	—	—	—	—
V–4.0 Ti–1.0 Si	V_3Si	261	none	>100	395	16	390	60
V–7.5 Ti–0.5 Si	V_3Si	266	none	>100	345	1	340	6
V–15.0 Ti–1.0 Si	V_3Si	341	none	>100	none	>100	375	6

A 100-g ingot of each of the alloys was melted in a nonconsumable arc melting furnace. Electron-gun-refined vanadium was used for the preparation of the alloys. The rest of the materials used for alloying are listed in Table II.

The pancake ingots were sandblasted and pickled in dilute HNO_3 acid. The ingots

were canned in a stainless steel sheet, heliarc welded on the sides of the can, and evacuated through a tube incorporated into the assembly before sealing.

The approximately $\frac{1}{6}$-in. thick pancake ingots were broken down hot with 30 to 40 rolling passes to $\frac{3}{16}$-in. thick plates (~60% total reduction area on a two-high rolling mill). The rolling temperature was between 1350° and 1200°C.

After each 2 to 4 passes, the alloy was put back in a muffle furnace for reheating. After rolling, the stainless steel cans were removed and the hot-rolled sheets were sandblasted and pickled in dilute nitric acid.

In a second rolling operation the sheets were rolled approximately to $\frac{1}{16}$-in. thickness in 10 to 15 passes. The sheets were preheated to 650°C before rolling. The finished sheets were sandblasted and pickled again to remove the surface oxides.

Specimens ($\frac{1}{2} \times \frac{3}{8}$ in. platelets) were cut out from the rolled materials and encapsulated in quartz tubes which were then evacuated, partially filled with argon gas, solution annealed at 1300°C for 4 h, and water quenched.

Ageing treatments were carried out on the specimens at 550°, 650° and 750°C. The specimens were encapsulated in evacuated Vycor tubes if the ageing time exceeded 1 h. After the ageing treatment the specimens were water quenched. The specimens were mounted in bakelite, ground, and prepolished.

The ageing was followed by measurements of hardness variation. Vickers hardness tests were carried out, using the Vickers-pyramid indenter and 20 kg load.

The age hardening of the selected alloys

Table IV summarizes the most important data on the age hardening of the selected alloys.

Typical age-hardening curves, representing the hardening of one alloy composition of each ternary system, are presented in Figs. 23, 24, and 25.

From Table IV and Figs. 23, 24 and 25 it can be seen that the vanadium–titanium–oxygen alloys age faster than the vanadium–titanium–beryllium and vanadium–

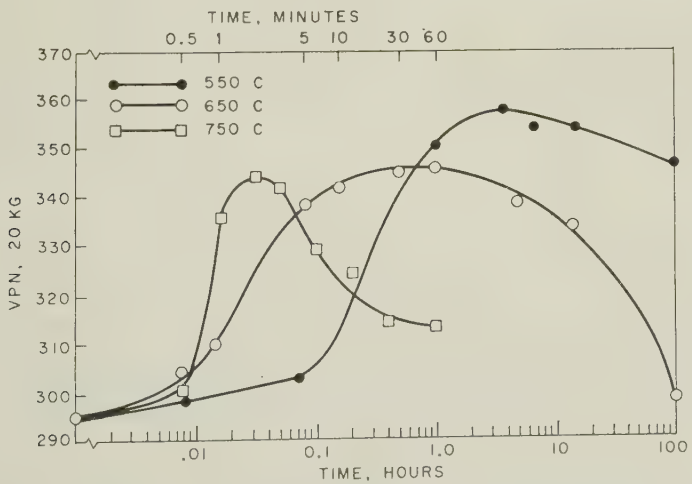

Fig. 23. V–10 wt. % Ti–0.14 wt. % O alloy. Water quenched from 1300°C and aged at 550°, 650°, 750°C. ● 550°C; ○ 650°C; □ 750°C.

titanium–silicon alloys. This is explained by the fact that the oxygen has relatively the smallest atomic size among the alloying elements in the systems investigated, and so its diffusivity is the highest.

Generally, the higher the ageing temperature was, the shorter the time required to obtain maximum hardness. An exception was the V–1.5 Ti–0.5 wt. % O alloy, which indicated higher hardening rate at 650° than at 750°C. But the hardening response of this alloy was not pronounced; approximately 30 VPN difference was found between the solution-annealed and the hardest aged conditions.

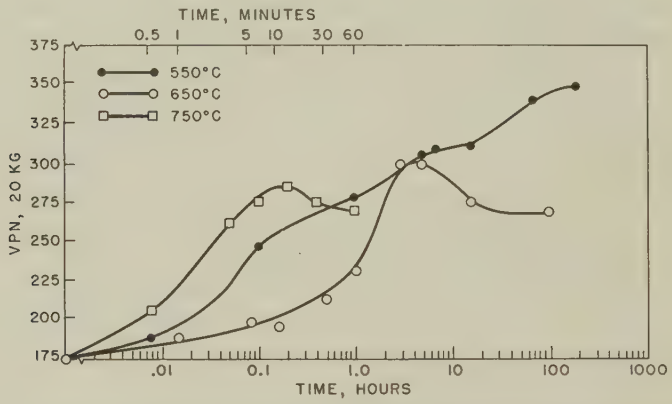

Fig. 24. V–1.0 wt. % Ti–0.5 wt. % Be alloy. Water quenched from 1300°C and aged at 550°, 650°, 750°C. Symbols as in Fig. 23.

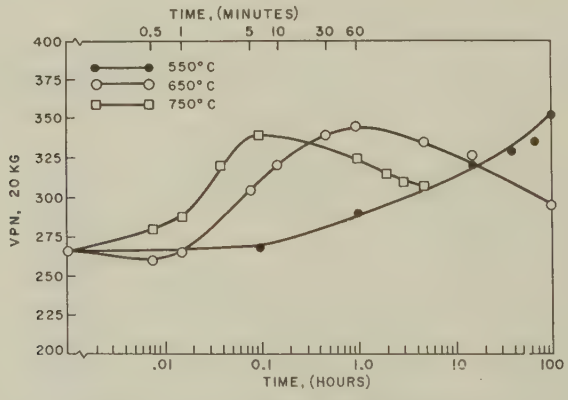

Fig. 25. V–7.5 wt. % Ti–0.5 wt. % Si alloy. Water quenched from 1300°C and aged at 550°, 650°, 750°C.

No data are presented on the age-hardening of alloy V–10.0 wt. % T–0.4 wt. % Be. This alloy exhibited extreme brittleness in both solution-annealed and aged condition, and cracking occurred during the indentation of the Vickers pyramid. The Vickers hardness of this alloy was not a function of the ageing time; it varied irregularly between 900 to 1000 VPN.

Potential age hardening was indicated by the vanadium–titanium–beryllium and

vanadium–titanium–silicon alloys. At the lower ageing temperatures these alloys harden considerably; at 550°C ageing temperature the maximum hardness was not even obtained during the longest ageing time applied (200 and 100 h, respectively).

The aged specimens were examined metallographically. The microstructures observed

Fig. 26. V–10.0 wt. % Ti–0.14 wt. % O alloy. Aged at 650°C for 100 h. Dispersed precipitate. (× 500)

contained a dispersed precipitate as second phase in the matrix. Figure 26 presents a typical microstructure of this kind. This photomicrograph was taken of alloy V–10.0 wt. % Ti–0.14 wt. % O after ageing for 100 h at 650°C. From Fig. 23 it is obvious that this alloy was considerably over-aged. In spite of the overageing, the dispersed precipitate still has a discrete size; no coagulation can be detected. This suggests that the hardening of the selected alloys is mostly due to the early stage of the precipitation process before a more intensive growth starts.

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REFERENCES

1 M. HANSEN, H. D. KESSLER AND D. J. MCPHERSON, *Trans. Am. Soc. Metals*, 44 (1952) 581.
2 R. F. DOMAGALA AND D. J. MCPHERSON, *Trans. AIME*, 200 (1954) 238.

[3] W. ROSTOKER AND A. YAMAMOTO, *Trans. Am. Soc. Metals*, 46 (1954) 1136.
[4] W. KÖSTER AND K. HAUG, *Z. Metallk.*, 48 (1957) 327.
[5] R. P. ELLIOT AND W. ROSTOKER, *Trans. Am. Soc. Metals*, 50 (1958) 617.
[6] P. GREENFIELD AND P. A. BECK, *Trans. Am. Soc. Metals*, 206 (1956) 265.
[7] H. L. LEVINGSTON AND B. A. ROGERS, *U.S. Atomic Energy Commission, Publs. AECD-3602 and ISC-340*, (1953).
[8] P. CHIOTTI, personal communication to LEVINGSTON AND ROGERS.
[9] H. K. ADENSTEDT, J. R. PEQUINOT AND J. M. RAYMER, *Trans. Am. Soc. Metals*, 44 (1952) 990.
[10] P. PIETROKOWSKY AND P. DUWEZ, *Trans. AIME*, 194 (1952) 627.
[11] M. HANSEN, E. L. KAMEN, H. D. KESSLER AND D. J. MCPHERSON, *Trans. AIME*, 191 (1951) 881.
[12] B. W. GONSER, *Ind. Eng. Chem.*, 42 (1950) 222.
[13] R. I. JAFFEE, personal communication to M. HANSEN, (October, 1950).
[14] C. M. CRAIGHEAD, O. W. SIMMONS AND L. W. EASTWOOD, *Trans. AIME*, 188 (1950) 485.
[15] J. L. HAM, *Trans. ASME*, 73 (1951) 723.
[16] E. PIPITZ AND R. KIEFFER, *Z. Metallk.*, 46 (1955) 187.
[17] D. J. MAYKUTH, H. R. OGDEN AND R. I. JAFFEE, *Trans. AIME*, 197 (1953) 231.
[18] D. SUMMERS-SMITH, *J. Inst. Metals*, 81 (1952/53) 73.
[19] O. N. CARLSON, D. T. EASH AND A. L. EUSTICE, in *Reactive Metals*, Metallurgical Society Conferences, Vol. 2, Interscience Publishers, New York, 1959, p. 277.
[20] R. P. ELLIOTT, discussion to ref. 19, *op. cit.*, p. 293.
[21] L. W. EASTWOOD, R. M. GOLDHOFF, J. W. HOLLADAY AND J. G. KURA, *Battelle Mem. Inst., AF Tech. Rept. 6515*, Part I, (June 1951).
[22] R. KIEFFER, K. SEDLATSCHEK AND H. BRAUN, *Z. Metalk.*, 50 (1959) 18.
[23] L. MISCH, *Metallwirtschaft*, 15 (1936) 163.
[24] A. V. SEYBOLT AND H. T. SUMSION, *Trans. AIME*, 197 (1953) 282.
[25] M. HANSEN, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
[26] H. J. WALLBAUM, *Z. Metallk.*, 31 (1939) 362.
[27] W. B. PEARSON AND W. HUME-ROTHERY, *J. Inst. Metals*, 80 (1952) 652.
[28] H. SCHACHNER, E. CERWENKA AND H. NOWOTNY, *Monatsh. Chem.*, 85 (1954) 245.
[29] H. J. WALLBAUM, *Z. Metallk.*, 33 (1941) 378.
[30] R. KIEFFER, F. BENESOVSKY AND H. SCHMID, *Z. Metallk.*, 47 (1956) 247.

THE DEVELOPMENT OF IMPROVED VANADIUM-BASE ALLOYS FOR USE AT TEMPERATURES UP TO 1800°F*

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SUMMARY

Vanadium-base sheet alloys containing titanium and/or columbium, molybdenum, tantalum, and tungsten exhibit excellent strength at elevated temperatures and weldability. Since oxidation protection was not an aim of this program, tensile and creep properties were determined in inert atmospheres. These alloys with outstanding cold fabricability are superior to the best nickel- and cobalt-base sheet materials on a density-corrected tensile strength basis at temperatures above 1500°F.

INTRODUCTION

Much of the previous work on vanadium has been performed at Armour Research Foundation. A three-year program initiated in 1951 established the basic phase equilibria and alloying behavior of vanadium[1]. This program was carried to the point of indicating the competitive position of vanadium with respect to titanium. Later results, corrected for vanadium's higher density, showed that the stress for 0.1% creep strain in 100 hours for simple alloys such as V–10Ti** and V–20Ti was 3 times higher than that for Ti–6Al–4V at 1000°F. A subsequent program was successful in the development of vanadium alloys for fuel element cladding for use at 1200° to 1470°F in sodium[2]. Mechanical properties were not maximized since other parameters had to be considered. Even so, dilute compositions such as V–2.5Ti–1 Si exhibited a 100-hour rupture life of 68,000 p.s.i. at 1200°F. The alloys were weldable, and formability was outstanding; some of the materials were cold rolled 98% and withstood a 180° 3t bend test after 88% reduction. One of the important observations was that the creep-rupture properties were very high as compared to the elevated-temperature tensile tests at the same temperature.

The further development of vanadium has been slow. A serious limitation to the use of vanadium has been the formation of liquid oxide (V_2O_5) in air at 1245°F. Preliminary studies are currently being conducted to develop coatings which offer protection against oxidation. The fact that vanadium possesses desirable strength properties to even higher elevated temperatures has heretofore been unrecognized. The 3560°F melting point was considered a sign of low softening temperature; however, this melting point places vanadium among the ten highest melting metals and

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** All compositions are reported in weight per cent.

slightly above chromium. In addition, a fact not often considered, vanadium has by far the lowest density of these highest melting point metals. Thus, vanadium alloy properties are even more promising on a density-corrected basis.

A current program for the Navy Bureau of Weapons was undertaken with the objective of improving elevated-temperature properties. As an initial phase of this alloy development program, the work reported here concerns a study of alloys of the V–Ti–Cb, V–Ti–Mo, V–Ti–Ta and V–Ti–W systems. Extensive solid solutions exist in these systems which offer promise of elevated-temperature strength. Titanium was included since it was considered a necessary addition to improve ductility, but the improvement in the vanadium purity has allowed the deletion of this solute; titanium has generally been useful for strengthening, however. Alloying behavior was established through tensile tests in neutral atmosphere at room temperature, 1200° and 1800°F. Preliminary aging and creep properties have also been evaluated at 1200°F for V–Ti–Cb alloys complexed with silicon or beryllium.

EXPERIMENTAL PROCEDURES

Materials and melting

The vanadium metal used in this investigation was purchased from Union Carbide Metal Company as minus $\frac{1}{4}$ in. mesh metal chips. The hardness as obtained on a test melt was 146 VHN or approximately $85R_B$. This vanadium metal compares very favorably in quality with vanadium previously offered as laboratory grade stock. The cost of this vanadium has been reduced from $80 per pound to $35 per pound recently, and further price reductions would be likely with increased production.

All alloying elements were 99.8% purity or better. The majority of alloys were prepared by nonconsumable arc-melting 200-gram "pancake" ingots of the desired composition. Additions of the elements molybdenum, tungsten, and tantalum were accomplished by adding premelted master alloys consisting of V–50Mo, V–50W, and V–50Ta. The first two were friable and readily crushed to $\frac{1}{8}$ mesh. The latter — although expected to be friable, being near a Laves phase — was ductile and cold rolled to 0.050 in. sheet.

The compositional limits of the alloys prepared ranged from 0 to 20% titanium, 0 to 50% columbium or tantalum, and 0 to 20% tungsten or molybdenum. Efforts to make alloys containing greater amounts of molybdenum and/or tungsten were discontinued since these alloys were difficult to fabricate to sheet.

Sheet fabrication

The majority of the pancake ingots were hot press forged and hot rolled at temperatures in the range 2100° to 2550°F. At these temperatures the formation of oxide upon the ingots was controlled by heating in an inert atmosphere, by encasing the ingot in a stainless steel sheath, or by limiting the time the ingot was exposed at temperature. After hot working, the oxide and/or sheath was removed, and the final working was accomplished by warm and then cold rolling to about 0.050 in. thickness. A limited number of alloys were also cold rolled to 0.050 in. sheet with only one intermediate anneal.

Evaluation

Sheet tensile specimens $2\frac{1}{4}$ in. long with a $\frac{1}{4}$ in. wide by $\frac{3}{4}$ in. long gage section were

employed. For creep testing, the specimens were $4\frac{3}{4}$ in. long with a gage section $\frac{1}{4}$ in. wide by $1\frac{1}{4}$ in. long. All the specimens were fully annealed and/or aged prior to testing.

A Hounsfield Tensometer of 2 metric ton capacity was used for all tensile testing. Creep testing was done in pan-loaded 20:1 lever machines. Elevated-temperature tests were performed in capsules which were continuously purged with helium. Thermocouples attached to each shoulder of the specimen insured uniform temperature throughout the gage length.

RESULTS

Sheet fabricability and weldability

Formability of vanadium alloys is outstanding. The only factor limiting fabrication of the small arc-cast pancake ingots was the ingot breakdown. With improved geometry and/or a better working process such as extrusion, initial hot working could be more readily accomplished. Even so, a large majority of the arc-cast ingots were successfully hot rolled, and all hot-worked material was subsequently rolled at least 50% at room temperature. The unusual ability of vanadium to preserve cold-working capability with large alloy additions was demonstrated by cold rolling V–50Ta and V–50Cb arc-cast ingots directly to sheet. The promising V–5Ti–20Cb alloy was cold rolled directly to sheet with only one intermediate anneal.

At similar solute levels, the compositions containing columbium and tantalum were more easily hot worked than alloys of molybdenum or tungsten. A ternary addition of titanium, particularly in larger amounts, improved workability. For example, the fabrication of V–5Ti–20W was difficult, but V–20Ti–20W was easily made into good sheet. The V–5Ti–20Cb alloy produced excellent sheet, whereas the quality of the V–(1, 2.5)Ti–20Cb material was marginal. Increasing the columbium level to V–5Ti–40Cb made working more difficult.

Further complexing of the highly fabricable V–5Ti–20Cb alloy with quaternary additions of 0.1–0.2% beryllium or 0.5–1% silicon resulted in materials that could not be cold worked initially. However, since these additions refined the as-cast grain size, they effectively improved the hot working characteristics. Compositions without these additions exhibited coarse columnar as-cast grains.

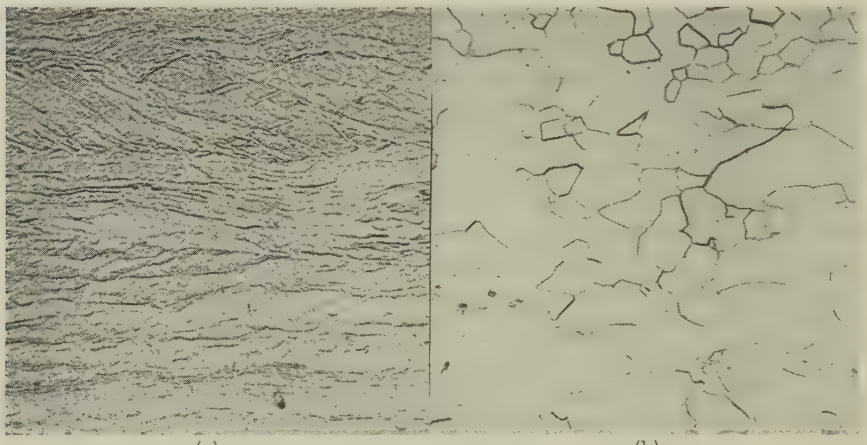
Weldability of these solid solution alloys can be expected to be very good. In order to substantiate the weldability, a cursory study was conducted on specimens for the V–5Ti–20Cb alloy. Joining was accomplished by tungsten-electrode, inert-gas techniques. Both sides of the sheet specimens were protected by a helium atmosphere. When tested in tension, all welded specimens failed in the heat-affected zone or the parent metal, and no serious degradation of properties was noted. Room-temperature tensile elongations of 15% were observed, as compared with 19% for the unwelded alloy.

Annealing and metallographic studies

Before the materials were tested, an annealing study was performed to determine the recrystallization temperatures. The alloys selected for the annealing studies were representative of the range of alloys fabricated to sheet — generally a comparatively dilute and a highly alloyed composition from each of the V–Ti–(Cb, Mo, Ta, W) series. Metallographic and hardness examination indicated an annealing treatment of

1800°F would be satisfactory for all the solid solution alloys (Fig. 1). The alloys containing a precipitate required $\frac{1}{2}$ h at 2000°F to recrystallize completely the as-worked structure.

The basic compositions studied were generally solid solution alloys. A literature



(a) (b)

Fig. 1. Cold worked and recrystallized structures for V–20% Cb. Etchant: 20% HF, 20% HNO_3, 60% glycerine. (a) As-rolled; (b) annealed 1830°F for 30 min and water-quenched.

survey indicated that extensive solubility of the solute elements in vanadium was to be expected[3]. Later experimental data[4] revealed that continuous series of solid solutions occur in the systems V–Ti–Cb, V–Ti–Mo, and V–Ti–W, whereas a two-phase region exists in the V–Ti–Ta system. Limited metallographic examinations on the program corroborated the existence of single-phase spaces. In fact, with the short annealing times employed, single-phase structures were noted for the V–(5, 10, 20)Ti–20 Ta alloys although a small amount of precipitate might be expected under equilibrium conditions. Precipitation of TaV_2 was observed in the V–50Ta material after tensile test at 1800°F, and caused brittleness.

Tensile results

Table I lists the results of the 0.050-in. sheet tensile specimens; the yield strength represents 0.2% offset. Some of the data for the vanadium-rich alloys are summarized in Fig. 2. All alloys are stronger than unalloyed vanadium and V–Ti-base compositions show improvement over the binary alloys.

Alloying behavior for the V–Ti–Ta system is shown in Fig. 3. Although the solid solution alloys are relatively weak at room temperature, they exhibit good retention of strength to elevated temperatures.

For the binary alloys, increasing the tantalum content from 10 to 20% resulted in improved strength and decreased ductility; the V–50Ta alloy was completely brittle when tested in the recrystallized condition. Further study on this composition was discontinued as metallographic investigations indicated the precipitation of a second phase (TaV_2). Alloying V–10Ta or V–20Ta with titanium resulted in improved room-temperature ductility and generally slightly improved room-temperature and 1200°F

tensile strength. At 1800°F, the amount of titanium added has a marked effect as noted at the V–20Ta level. Approximately 5% titanium improved the 1800°F strength; 20% titanium additions were detrimental and caused the ternary alloy to be weaker than the binary composition.

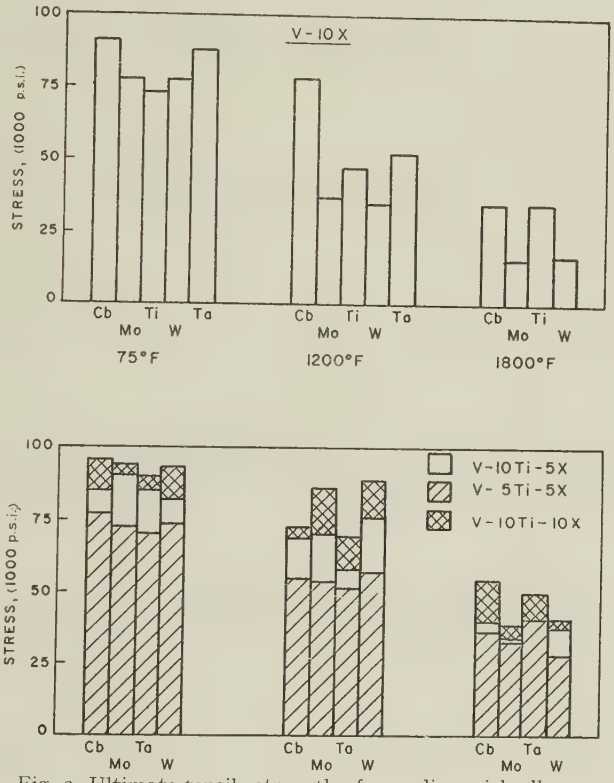


Fig. 2. Ultimate tensile strength of vanadium-rich alloys.

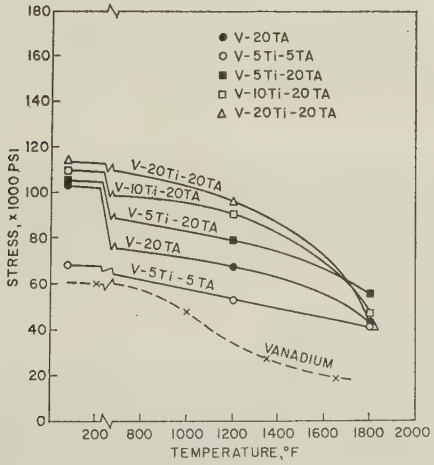


Fig. 3. Ultimate tensile strength of V–Ti–Ta alloys.

TABLE I

TENSILE PROPERTIES OF VANADIUM SHEET ALLOYS

Annealed 1/2 h at 1830°F, Water quenched

Alloy (wt. %)	Room temperature			1200°F			1800°F		
	Ultimate tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elong. (%)	Ultimate tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elong. (%)	Ultimate tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elong. (%)
10Ti	73,500	65,200	29	46,700	34,800	32	35,800	34,000	36
10Mo	78,900	74,000	13	39,100	37,300	—	17,700	16,000	51
10W	78,200	73,600	9	37,900	34,900	13	19,100	15,200	2[a]
20W	103,000	102,000	0	71,300	58,600	11	26,700	23,500	14
10Cb	92,100	85,000	21	77,800	51,700	—	36,800	33,900	41
20Cb	107,000	105,500	6	81,700	61,200	13	55,100	41,500	22
50Cb	168,000	163,000	2	151,000	130,300	3	85,300	75,400	5
10Ta	89,200	85,500	11	53,500	42,200	10	—	—	—
20Ta	103,000	89,000	8	65,000	57,000	—	—	—	—
50Ta[b]	216,000	160,000	4	154,000	143,000	7	42,100[c]	—	—
5Ti–5Mo	71,800	55,500	25	54,800	42,800	—	32,900	29,600	19
10Ti–5Mo	89,700	82,700	22	68,900	47,000	—	34,600	32,400	28
10Ti–10Mo	91,200	79,400	13[a]	82,800	56,100	11	39,100	34,500	9
20Ti–5Mo	100,000	91,900	19	79,500	63,400	—	42,800	38,100	29
20Ti–10Mo	114,000	104,500	23	90,800	67,800	17	43,500	39,900	42
5Ti–20Mo	93,500	80,300	4	—	—	—	44,300	39,400	3
5Ti–5Cb	77,200	59,700	25	55,300	41,600	—	36,500	32,100	27
5Ti–10Cb	87,800	72,500	25	70,600	46,400	—	47,800	44,600	12
5Ti–20Cb	106,200	97,700	19	86,800	68,200	—	69,500	63,000	10[a]
10Ti–5Cb	84,200	70,400	27	67,800	50,000	—	39,700	35,000	39
10Ti–10Cb	94,400	77,500	21	71,900	60,700	—	52,700	48,500	6[a]
10Ti–20Cb	111,200	102,000	23	94,000	67,700	16	54,000	51,400	18
20Ti–10Cb	110,000	99,700	20	99,300	74,300	17	43,200	40,300	54
20Ti–20Cb	113,500	108,500	21	96,500	78,500	12	44,200	41,300	56

TABLE I (continued)

Alloy (wt. %)	Room temperature			1200°F			1800°F		
	Ultimate tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elong. (%)	Ultimate tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elong. (%)	Ultimate tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elong. (%)
5Ti–20Cb–0.5Si[d]	157,000	151,000	5	135,400	115,100	8	—	—	—
5Ti–20Cb–0.5Si[e]	144,000	142,000	3	—	—	—	—	—	—
5Ti–20Cb–1Si[f]	136,000	122,300	21	131,000	92,400	8[a]	37,200	34,200	74
5Ti–20Cb–1Si[d]	187,000	178,200	3	147,500	116,200	6	—	—	—
5Ti–5Ta	69,600	53,500	29	52,700	39,100	—	41,700	38,900	17
5Ti–10Ta	85,000	69,800	23	67,600	44,700	—	49,300	41,500	12
5Ti–20Ta	105,000	83,200	25	79,400	61,700	—	55,300	47,000	8
10Ti–5Ta	84,300	70,900	17	59,200	48,300	—	41,200	36,300	19
10Ti–10Ta	89,300	75,900	22	71,500	53,900	—	49,300	36,200	25
10Ti–20Ta	110,000	106,000	7	90,700	62,300	13	47,000	42,700	18
20Ti–20Ta	113,500	107,500	18	95,700	74,500	13	41,000	39,700	85
5Ti–5W	73,600	57,000	23	58,500	39,800	—	28,900	24,800	7[a]
5Ti–10W	85,900	76,500	23	74,300	51,200	17	39,300	36,600	13[a]
10Ti–5W	80,000	69,300	23	76,200	48,200	—	37,800	33,100	10
10Ti–10W	89,300	73,400	22	86,100	57,300	7	41,300	36,300	9
10Ti–20W	107,500	101,800	19	94,800	63,900	15	46,600	41,400	17
20Ti–10W	111,600	106,000	25	94,000	68,900	17	43,500	38,500	80
20Ti–20W	112,000	105,200	21	108,000	82,000	12	46,400	41,600	52

[a] Broke near gage mark.
[b] As-rolled.
[c] Brittle fracture, broke during elastic loading.
[d] Annealed 2010°F, 1/2 h, water quenched.
[e] Aged 100 h at 1200°F.
[f] Annealed 2000°F, 1 h, aged 100 h at 1200°F, stressed 100 h at 1200°F.

Results for the V–Ti–Cb and V–Ti–Ta series alloys showed similar trends; that is, columbium increases strength, but titanium must be limited for high-temperature strength. Unlike V–50Ta, the alloy V–50Cb was ductile when tested in the recrystallized condition. In general, the alloys of this series exhibited the best retention of strength to elevated temperatures.

Figure 4 illustrates the alloying behavior for the system V–Ti–W; similar behavior was noted for the system V–Ti–Mo. Because of difficulties experienced in fabricating sheet materials, alloys of this series were not evaluated as extensively. The results

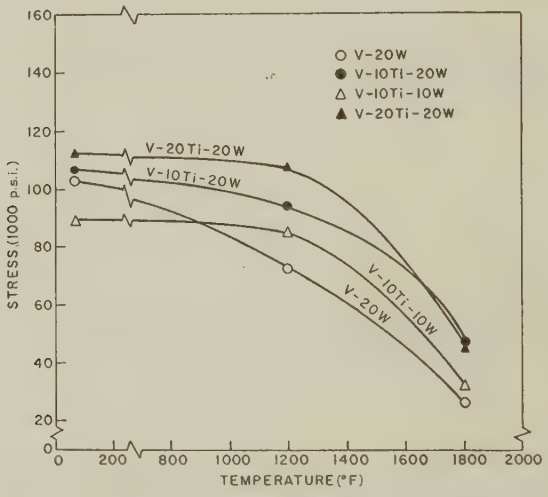


Fig. 4. Ultimate tensile strength of V–Ti–W alloys.

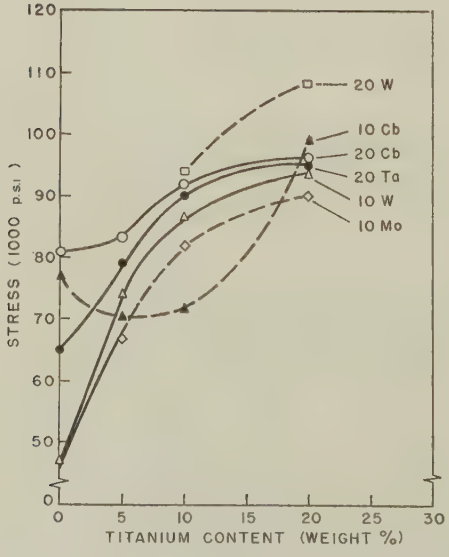


Fig. 5. Influence of titanium on the 1200°F tensile strength of V–(Cb, Mo, Ta, W) alloys.

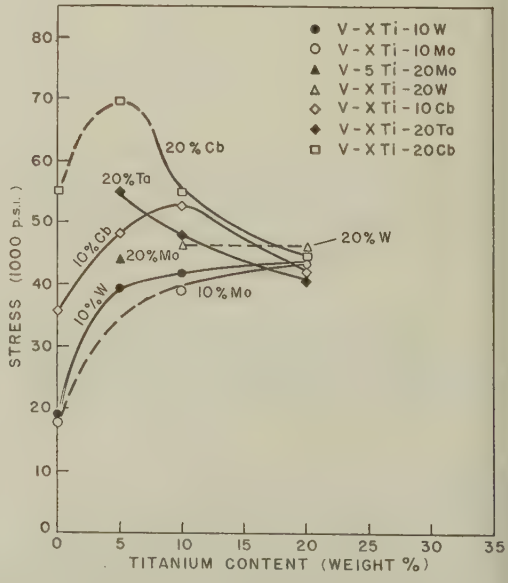


Fig. 6. Influence of titanium on the 1800°F tensile strength of V–(Cb, Mo, Ta, W) alloys.

obtained are similar to those for the V–Ti–Ta system with respect to titanium. The slope for the strength *versus* temperature curves is greater for the V–Ti–Mo and V–Ti–W than for V–Ti–Cb, suggesting that columbium is the most potent strengthener.

A more concise illustration of the influence of titanium upon the 1200° and 1800°F strength for the various systems is illustrated in Figs. 5 and 6, respectively. As seen in Fig. 5, the strength is dependent upon total alloying content and no definite trend is noted with respect to the refractory metal additions. Increasing titanium content up to 20% improved 1200°F strength. At 1800°F (Fig. 6), equal strengths are noted for the V–Ti–Mo and V–Ti–W systems at 10 or 20% titanium levels. Similar to the V–Ti–Cb materials, titanium contents above 5 or 10% are detrimental with V–Ti–Ta alloys.

Age-hardening studies

Additions of 0.1 – 0.5% beryllium 0.5 – 1% silicon were added to the V–5Ti–20Cb base with the objective of producing age-hardenable alloys with improved strength for 1200°F application. Also, since titanium appears to be useful for 1200°F strengthening, the compositions V–20Ti–10Cb–(0.5, 1.0)Si and V–10Ti–0.2Be were prepared and evaluated for age hardening characteristics. Materials containing more than 0.2% beryllium could not be fabricated to sheet, while all the silicon-bearing materials exhibited good fabricability. Specimens from these compositions were solid-solution

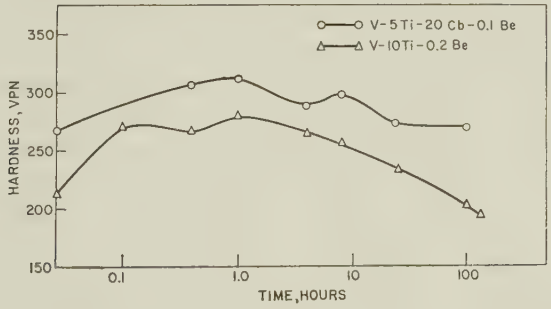


Fig. 7. Aging response at 1200°F for vanadium-rich alloys containing beryllium.

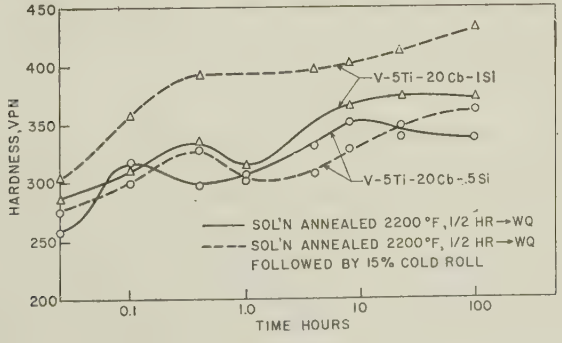


Fig. 8. Aging response at 1200°F for V–Ti–Cb–Si alloys.

annealed at 2000°F and then aged at 1200°F for times ranging from 0.1 h to 120 hours. Typical aging curves are shown in Figs. 7 and 8. The alloys with high titanium–silicon ratios exhibited no age-hardening propensities.

Both of the beryllium-containing alloys rapidly overaged and, in fact, exhibited equal or lower hardness after aging for 100 hours (Fig. 7). Microstructurally, the alloys had a well-dispersed, fine precipitate after aging for 8 hours and did not materially change in appearance thereafter. Similar metallographic results were noted for the V–5Ti–20Cb(0.5, 1.0)Si alloys (Fig. 8) although these alloys did not overage in 100 h at 1200°F like the beryllium-bearing alloys.

On the basis of the aging data, the silicon-containing compositions were considered the most promising and therefore were evaluated for room temperature and 1200°F tensile strength. The tensile results (Table I) showed a substantial improvement over the basic solid solution alloys.

1200°F creep evaluation

The objective of the 1200°F creep tests was to determine if the vanadium alloys are equivalent, on a density-corrected basis, to the best available sheet materials. Stress to produce 0.1% total plastic deformation in 100 h was the criterion. A literature survey was performed, and from the published information one of the best materials is Udimet 500; the 100-h, 0.1% deformation stress is 90,000 p.s.i.[5]. To be competitive on a density-corrected basis, the required stress level for the vanadium alloys is about 65,000 p.s.i.

Several vanadium alloys were evaluated for creep resistance at 1200°F. When loaded to stress levels competitive with the best available contemporary sheet materials, failure occurred in a short time interval. This poor strength for annealed solid solution vanadium alloys is not surprising. The only other evaluations to date were for aged V–5Ti–20Cb 1Si and V–5Ti–20Cb–0.5Si specimens. The stress to produce 0.1% plastic deformation in 100 h at 1200°F was 50,000 p.s.i. for the alloy V–5Ti–20Cb–1Si, representing a significant improvement over the V–5Ti–20Cb solid solution. However, this alloy embrittled during the stressed exposure. The V–5Ti–20Cb–0.5Si alloy exhibited 1% plastic deformation under similar conditions, and did not embrittle during exposure.

Microexamination of the stressed V 5Ti 20Cb–1Si alloy revealed that the stress-induced brittleness was caused by the nucleation of silicides in the grain boundaries and the path of fracture originated in these grain boundaries. The employment of an intermediate working operation prevented the formation of this envelope, but the specimens exhibited excessive hardening (Fig. 8).

Comparative properties

Figure 9 shows the tensile strengths of three of the more promising vanadium alloys as compared with various high-temperature sheet materials. The vanadium alloys offer greatest promise through retention of strength to elevated temperatures. At room temperature the precipitation-hardened stainless steels, Udimet 600, and titanium alloy have higher strength than the vanadium alloys[6,7,8]. Above 1000°F the stainless steels and titanium alloy rapidly lose strength. Udimet 600 is among the materials which possess good strength in this temperature range. However, at 1200°F Udimet 600 begins to lose strength rapidly and at 1500°F the vanadium

alloys begin to show superiority. Tensile data at 1800°F show that the vanadium alloys have considerable strength. In fact, at this temperature the vanadium alloys are superior to other refractory materials such as molybdenum[9] and columbium base alloy[10], on a density-corrected basis. These latter materials are not shown in Fig. 9.

Although the vanadium alloys exhibit excellent strength in the temperature range

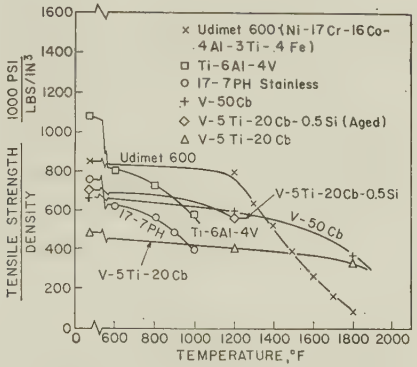


Fig. 9. Density-corrected ultimate tensile strength of moderate temperature alloys.

1500° to 1800°F, they are not oxidation-resistant. It appears that good strength may be retained above 1800°F, and at these temperatures the competitive refractory alloys are also not oxidation-resistant. All of the compositions studied are single-phase solid solution alloys with the exception of V–Ti–Cb–Si, and do not represent the optimum results to be expected. Further complexing can certainly be performed at a slight loss in ductility since adequate ductility is exhibited by the promising base compositions.

SUMMARY AND CONCLUSIONS

Preliminary screening evaluations on arc-cast V–Ti–(Cb, Mo, Ta, W) materials have shown the alloying behavior of titanium and the refractory metal additions. Of the refractory metal additions studied, columbium is the most potent strengthener, particularly on a density-corrected basis. Titanium in amounts of 5–10% increased the tensile strength at elevated temperatures with an improvement in room-temperature ductility; 20% titanium is detrimental to 1800°F strength. All elevated temperature testing was performed in inert atmosphere because of lack of oxidation resistance.

The majority of the materials studied were solid solution alloys and, though relatively weak at room temperature, exhibited excellent retention of strength to elevated temperatures. For instance one of the more promising alloys, V–5Ti–20Cb, in the fully recrystallized condition exhibited an ultimate tensile strength of approximately 70,000 p.s.i. at 1800°F. On a density-corrected tensile strength basis this alloy began to show superiority over the commercial nickel- and cobalt-base "super-alloys" at approximately 1500°F. In addition, the vanadium alloy exhibits 19% room-temperature tensile elongation and can be cold rolled to reduction of over 90%

once the as-cast structure is modified. The material is weldable by tungsten-electrode, inert-gas techniques.

These alloys do not represent the optimum results to be expected. Further improvements can certainly be expected with the incorporation of solid solution, age hardening (1200°F application), and dispersion strengthen-additions. Some reduction in ductility can readily be tolerated since most of the vanadium compositions exhibited a room-temperature tensile elongation in excess of 20%. Limited studies were conducted to develop silicon- or beryllium-bearing age hardening alloys, and although no alloy was found to be competitive with the best commercial alloy, the results showed promise. The addition of 0.5% silicon to the V–5Ti–20Cb alloy produces age hardening effects that are metastable for over 100 h at 1200°F. After an aging treatment that results in 5% room temperature tensile elongation, the ultimate tensile strength at room temperature is increased by 50%, and the 1200°F creep-resistance is improved. All of these data presented are the result of preliminary programs, and work is continuing.

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REFERENCES

1 A. S. YAMAMOTO, W. ROSTOKER, D. J. MCPHERSON AND M. HANSEN, Exploration of vanadium-base alloys, *WADC Tech. Rept. 52–145*, Parts 1 (July 1952), 2 (November 1954), and 3 (January 1955).
2 R. J. VAN THYNE, Development of vanadium alloys for reactor application, Part II, Mechanical properties, in *Reactive Metals*, Metallurgical Society Conference, Vol. 2, Interscience Publ., Inc., New York, 1959.
3 W. ROSTOKER, *The Metallurgy of Vanadium*, 1st edn., John Wiley and Sons, Inc., New York, 1958, p. 46–65.
4 S. A. KOMJATHY, R. H. READ AND W. ROSTOKER, Phase relationships in selected binary and ternary vanadium-base alloy systems, *ARF Final Report to WADC under Contract No. AF 33(616)-5771*, July 1959.
5 *Udimet 500, Technical and Engineering Data*, Utica Metals Division, Kelsey-Hayes Company, New York.
6 The new stainless steels, *Materials and Methods*, April, 1956, p. 137–151.
7 *Udimet 600 – Preliminary Data*, Utica Metals Division, Kelsey-Hayes Company.
8 Ti–6Al–4V, *Titanium Engineering Bulletin No. 1*, Titanium Metals Corporation of America.
9 Physical and mechanical properties of molybdenum and the Mo–0.5 Ti alloy, *Defense Metals Information Center Memorandum 14*, Battelle Memorial Institute, April 10, 1959.
10 *Recent Advances in Columbium Alloys*, Applied Research Operation, Flight Propulsion Laboratory Department, General Electric Co., July, 1959.

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